All-electron fully relativistic Kohn–Sham theory for solids based on the Dirac–Coulomb Hamiltonian and Gaussian-type functions

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First-principle predictions of electronic structure and properties of solid-state materials containing heavy elements pose numerous challenges to computational methods, as variational treatment of relativistic effects is in many cases required and because multiple wave-function components coupled by the spin–orbit interaction increase the complexity of the formalism and the computational cost. Here, we present the first full-potential method for solids and surfaces that solves the fully-relativistic 4-component Dirac–Kohn–Sham equation within the framework of atom-centered Gaussian-type orbitals (GTOs), thus also allowing for a seamless transition to the methodology commonly used studies of molecules with heavy elements. We provide a detailed description of how key components of such a method are altered in the 4-component scheme, and show the necessary steps that need to be overcome when employing GTOs on periodic systems. Finally, we demonstrate the validity of the method on 3-dimensional silver halide (AgX) crystals with strong scalar-relativistic effects, and 2-dimensional honeycomb structures (silicene and germanene) exhibiting the quantum spin Hall effect.

I. INTRODUCTION

Relativistic effects on band structures and properties of solids containing heavy elements have for a long time been known to have a significant impact on both core and valence electrons.[1] The effects of relativity on the spectroscopic properties of electrons close to the nuclei (X-ray spectroscopy) were studied as early as in 1933.[2] In contrast, the importance of relativistic effects on valence states located close to the Fermi level was not apparent until 1957[3] when Mayers observed a large relativistic contraction of the 6s orbital and a corresponding expansion of the 5d orbital in heavy elements such as mercury. Such changes in the size of the atomic orbitals due to relativity can lead to dramatic changes in the structural and physical properties of solids.[4–6] For instance, Christensen demonstrated that these relativistic effects are responsible for the stable phase of lead being the face-centered cubic (FCC) crystal structure, in contrast to the diamond-like structure adopted by other group 14 elements (C, Si, Ge and Sn).[4] It has also been shown that relativistic effects need to be included in theoretical models of solids in order to explains why the ground state of CsAu is insulating and not metallic.[7] Relativity have also been shown to significantly increase the voltage of the lead-acid-battery reaction used in car batteries by 1.7-1.8 V out of the total 2.13 V,[8] and lead to a decrease in the melting temperature of mercury by 105 K,[9] making mercury the only metal that is liquid at room temperature. A protruding manifestation of relativity in quantum mechanics – the spin–orbit coupling (SOC) – leads to a splitting of bands in materials lacking space inversion symmetry.[10–12] These splittings can be remarkably large in transition-metal dichalcogenides,[13–16] and are then often referred to as "giant SOC". SOC plays a paramount role in the field of spintronics,[17–19] topological insulators,[20,21] and related spin-Hall effects.[22–24]

SOC has also been shown to open the band gap in 2-dimensional honeycomb systems[25–28] and change the stable phase of Flerovium (Fl, element 114) from FCC to a hexagonal close packed (HCP) structure.[29]

Materials exhibiting some of the unique properties mentioned above are rare,[30] however, and the search for novel materials must be aided by first-principle calculations.[31] Modeling spin–orbit-coupled solid-state systems is far from straightforward, and at the fully-relativistic level of theory with variationally included SOC, Kohn–Sham (KS) density functional theory (DFT)[32,33] is today the only affordable first-principle method for such studies due to its very favorable compromise between accuracy and computational feasibility. However, we note the promising recent works of Sakuma *et al.*[34] and Scherpelz *et al.*[35] at the GW level of theory.

A critical choice in the modeling of solids is the representation of the one-particle basis functions. There are two major families of basis sets: local functions (*e.g.* atom-centered orbitals) and plane waves. Plane waves are ill-suited to capture rapid oscillations of wave functions in regions close to the nuclei, and are for this reason often combined with pseudopotentials.[36] For heavier elements, these pseudopotentials can be constructed from relativistic all-electron calculations.[37,38] The use of pseudopotentials sacrifices the possibility to model the nodal structure of the wave functions close to the nuclei and introduces uncontrollable transferability errors. This makes all-electron methods in some cases the preferred method, *e.g.* for calculations of nuclear magnetic resonance (NMR) shifts.[39]

Relativistic all-electron calculations are possible using the relativistic Korringa–Kohn–Rostoker (KKR) method[40–43] or by extending Slater's augmented plane-wave (APW) method[44] to the Dirac Hamiltonian.[45,46] The APW method divides space into spheres centered at atoms and an interstitial region, and requires solving

a secular energy-dependent equation for each band to match KS orbitals at boundaries of the spheres. This approach results in equations with a nonlinear dependence on energies. The method is very accurate, but computationally expensive. To mitigate the computational cost, the APW method can be linearized,[47,48] leading to the linear-APW (LAPW) and linear muffin-tin orbitals (LMTO) methods, enabling the use of a full potential for all electrons. The LMTO approach has been extended to the relativistic domain [49–52]. Relativistic extension of LAPW was first developed by MacDonald *et al.*[53] and later by Wimmer *et al.*.[54] MacDonald *et al.* included SOC by a two-step variational method, the so-called second-variational approach, *i.e.* as a post processing to the spin-non-polarized scalar-relativistic self-consistent procedure. This process is performed on a smaller set of scalar-relativistic eigenfunctions, thus reducing the computational effort considerably. The second-variational approach was later extended and implemented in some of the modern program packages,[55–57] where the second-variational inclusion of SOC can be employed both self-consistently as well as non-self-consistently.

Both the full-potential LMTO and LAPW methods suffer from limitations when treating systems with deep-lying valence and extended core states.[58] If SOC is included, severe convergence problems can be encountered.[59] These limitations are due to the insufficient flexibility of the finite scalar-relativistic basis set for describing Dirac $p_{1/2}$ states in the core region.[53,59] Convergence is achieved when the basis is augmented with Dirac $p_{1/2}$ local orbitals in the second variational step.[60–62] Huhn and Blum carried out a benchmark study and a comparison of various LAPW strategies for the evaluation of the SOC contribution.[62]

More recently, the linearized methods were generalized by Blöchl to include the pseudopotential approximation, establishing the projector augmented wave (PAW) technique.[63,64] PAW introduces pseudopotentials as a well-defined approximation, and hence brings transferability errors under control, enabling all-electron calculations of properties in a pseudopotential framework. However, the complexity of the PAW approach makes its extension to *e.g.* include hybrid density functionals and the study of response properties difficult. A fully relativistic PAW method for both Dirac-type (4-component) and Pauli-type (2-component) equations was formulated by Dal Corso.[65]

An alternate strategy to the use of plane waves, is to expand the KS orbitals in a set of local functions. Such full-potential methods employing numerical orbitals have been extended to include scalar relativistic corrections,[66,67] as well as 4-component (4c) SOC.[68–71] Alternatively, basis functions can be constructed by placing analytic Slater-type orbitals (STOs) or Gaussian-type orbitals (GTOs) on atom centers. 2-component (2c) techniques using STOs were implemented by Philipsen *et al.*[72,73] and Zhao *et al.*[74] Relativistic calculations on solids with GTOs were reported with scalar-relativistic corrections,[75,76] as well as approximate 2c schemes solving Pauli-type equations,[77,78] or approaches based on using the Douglass–Kroll–Hess Hamiltonian.[79,80] While calculations that include scalar-relativistic corrections on solids are common,[66,67,75,76] the inclusion of SOC in non-relativistic implementations poses severe methodological complications due to the appearance of multiple spinor components of the wave functions as well as the need to use complex algebra.

We here present the first fully-relativistic all-electron full-potential GTO-based method, directly solving the 4c Dirac–Kohn–Sham (DKS) equation for solid-state systems while treating SOC variationally during the self-consistent optimization procedure. The approach builds on a transparent and efficient quaternion-based formulation of the 4c method employing a Kramers-restricted basis. The variational treatment of SOC is mandatory in studies of materials containing heavy elements, where SOC splittings are of the same magnitude as the effects of the crystal potential, and for which the evaluation of perturbational or non-self-consistent SOC can be insufficient.[34,62,81]

Our approach builds on previous nonrelativistic methods for handling periodic systems with GTOs. This includes the pioneering works of Pisani, Dovesi *et al.*[82–84] and a recent implementation of Łazarski *et al.*,[85] that we have combined with integral screening techniques utilizing quaternion algebra[86,87] as implemented in the 4c RESPECT program package.[88] In contrast to plane waves, GTOs can treat both core and valence electrons on an equal footing, the quality being independent on a fixed linearization energy. We will demonstrate that GTOs are a convenient and computationally efficient approach for full-potential relativistic calculations. The local nature of the GTOs makes them amendable to highly efficient linear scaling techniques, as the GTOs better reflect decay properties of operators and density matrices.[89] In addition, because periodicity is embedded explicitly in the local basis, systems that are periodic in 1 or 2 dimensions (polymers and slabs) can be studied using atom-centered GTOs while avoiding the requirement to repeat the polymer or slab in the non-periodic dimensions.[90] This eliminates the concern in calculations on such systems using plane waves that there will be spurious self-interactions between the system studied and its periodic images.

The rest of the paper is organized as follows: In Section II we establish the main principles of our 4c GTO-based method for the solid state. In Section II A we concentrate on the general formulation of the working equations, in Section II B we define the 4c density and the density matrix in real-space GTOs, Section II C shows consequences of the time-reversal symmetry on the structure of operators in both real space and reciprocal space, and these concepts are further developed in Section II D in a quaternion formulation. In Section II E we derive how the Coulomb potential and energy are evaluated using the 4c real-space GTOs, before we in Section II F analyze the problem of the long-range electrostatic lattice sums, and

describe its solutions within our theoretical framework. In Section II G we derive the exchange–correlation contributions. Practical implementation details and approximations required in realistic calculations are described in Section III. Results for the silver halide crystals and the 2-dimensional hexagonal structures are shown and discussed in Section IV, before we in Section V give some concluding remark and an outlook.

II. THEORY

A. General framework

In this section we outline the basic GTO-based scheme we use to solve the 4c DKS equations for periodic systems. Unless otherwise stated, we employ atomic units, setting the elementary charge e, the electron rest mass m_e and the Planck's constant $\hbar$ to unity. Throughout this paper, Einsteins's implicit summation over repeated indices will be used.

The fundamental building units are the scalar atom-centered normalized primitive Cartesian GTOs[91,92]

$$g_\mu(\boldsymbol{r}) \equiv \mathcal{N}(x - A_x)^{l_x}(y - A_y)^{l_y}(z - A_z)^{l_z} e^{-\alpha(\boldsymbol{r}-\boldsymbol{A})^2}, \ (1)$$

where $\mathcal{N}$ is the normalization constant, $\boldsymbol{\alpha}$ is the Gaussian exponent, $\boldsymbol{l} \equiv (l_x, l_y, l_z)$ is the Cartesian angular momenta, and $\boldsymbol{A}$ and $\boldsymbol{r}$ are the nuclear and electron coordinates, respectively. Basis representations of the solutions to the DKS equations is constructed in three steps. First, 4c basis bispinors χ_μ for a reference unit cell are formed

$$\chi_\mu(\boldsymbol{r}) \equiv \begin{pmatrix} \chi_\mu^L(\boldsymbol{r}) & 0_2 \\ 0_2 & \chi_\mu^S(\boldsymbol{r}) \end{pmatrix}, \tag{2}$$

using 2c spinors χ_μ^L and χ_μ^S defined for the so-called large (L) and small (S) components, respectively, as

$$\chi_\mu^L(\boldsymbol{r}) \equiv \mathbb{I}_2 \otimes g_\mu(\boldsymbol{r}), \tag{3a}$$

$$\chi_\mu^S(\boldsymbol{r}) \equiv \frac{1}{2c}(\boldsymbol{\sigma} \cdot \boldsymbol{p})g_\mu(\boldsymbol{r}), \tag{3b}$$

where $\mathbb{I}_2$ is the 2×2 identity matrix, $\boldsymbol{\sigma}$ are the Pauli matrices, $\boldsymbol{p} \equiv -i\boldsymbol{\nabla}$ is the electron momentum operator, and c is the speed of light. The construction of the small-component basis in Eq. (3b) utilizes the restricted kinetically balanced (RKB) condition which is essential to achieve variationally stable 4c solutions in a finite basis.[93] Second, the basis for periodic systems is obtained by translating χ_μ from the reference unit cell to the unit cell $\boldsymbol{m}$ as

$$\chi_{\mu\boldsymbol{m}}(\boldsymbol{r}) \equiv \chi_\mu(\boldsymbol{r} - \boldsymbol{m}), \tag{4}$$

where the unit cell position vector $\boldsymbol{m}$ is

$$\boldsymbol{m} = m^i \boldsymbol{a}_i, \qquad m^i \in \mathbb{Z}, i = 1, \dots, d. \tag{5}$$

Here, $\mathbb{Z}$ denotes the field of integers, d is the number of periodic dimensions, and $\boldsymbol{a}_i$ are the primitive vectors that constitute a Bravais lattice. Since all unit cells are equivalent, we choose the central unit cell $\boldsymbol{m} = \boldsymbol{0}$ to be the fixed reference unit cell. Third, symmetry-adapted Bloch functions for each $\boldsymbol{k}$-point from the first Brillouin zone $\mathcal{K}$ are constructed from the real-space GTOs as the Fourier series

$$\varphi_\mu(\boldsymbol{k}; \boldsymbol{r}) = \frac{1}{\sqrt{|\mathcal{K}|}} \sum_{\boldsymbol{m}} e^{i\boldsymbol{k}\cdot\boldsymbol{m}} \chi_{\mu\boldsymbol{m}}(\boldsymbol{r}), \tag{6}$$

where the infinite lattice sum is over the whole Bravais lattice. $|\mathcal{K}|$ is the volume of the primitive reciprocal unit cell (first Brillouin zone), and enters the normalization constant to ensure an approximate normalization of the Bloch functions. The symmetry-adapted functions in Eq. (6) satisfy the Bloch condition

$$\varphi_\mu(\boldsymbol{k}; \boldsymbol{r} + \boldsymbol{m}) = e^{i\boldsymbol{k}\cdot\boldsymbol{m}} \varphi_\mu(\boldsymbol{k}; \boldsymbol{r}), \tag{7}$$

by construction, and $\varphi_\mu(\boldsymbol{k}; \boldsymbol{r})$ can thus be used as basis functions that block-diagonalize a translationally invariant Hamiltonian.

Our aim is to solve the 4c DKS equations

$$\hat{F}\psi_p(\boldsymbol{k}; \boldsymbol{r}) = \varepsilon_p(\boldsymbol{k})\psi_p(\boldsymbol{k}; \boldsymbol{r}), \tag{8}$$

for each band p. Here $\varepsilon_p(\boldsymbol{k})$ and $\psi_p(\boldsymbol{k}; \boldsymbol{r})$ are the energy and the crystalline orbital (CO) of the p-th band, respectively, and $\hat{F}$ is the 4c Fock operator

$$\hat{F} = \begin{pmatrix} V(\boldsymbol{r}) & c\boldsymbol{\sigma} \cdot \boldsymbol{p} \\ c\boldsymbol{\sigma} \cdot \boldsymbol{p} & V(\boldsymbol{r}) - 2c^2 \end{pmatrix}, \tag{9}$$

consisting of the one-electron Dirac Hamiltonian[94] and the potential $V(\boldsymbol{r})$, which in the context of KS DFT contains the mean-field Coulomb potential and the exchange–correlation potential.[95–97] Such an approach approximates the two-electron interaction with an instantaneous Coulomb operator, neglecting the relativistic corrections to the electron–electron interaction. We expand the solutions $\psi_p(\boldsymbol{k}; \boldsymbol{r})$ of Eq. (8) in terms of the Bloch functions in Eq. (6):

$$\psi_p(\boldsymbol{k}; \boldsymbol{r}) = \varphi_\mu(\boldsymbol{k}; \boldsymbol{r})c^\mu{}_p(\boldsymbol{k}), \tag{10}$$

where $c^\mu{}_p(\boldsymbol{k})$ are the 4c CO expansion coefficients. Inserting the expansions in Eqs. (10) and (6) into Eq. (8), multiplying the equation with $\varphi_{\mu'}^\dagger(\boldsymbol{k}; \boldsymbol{r})$ from the left and integrating over spatial coordinates $\boldsymbol{r}$, yields the matrix form of the DKS equation in reciprocal space

$$F(\boldsymbol{k})c(\boldsymbol{k}) = S(\boldsymbol{k})c(\boldsymbol{k})\varepsilon(\boldsymbol{k}), \tag{11}$$

where $\varepsilon(\boldsymbol{k})$ is the diagonal matrix of the band energies. $F(\boldsymbol{k})$ and $S(\boldsymbol{k})$ are reciprocal-space forms of the Fock and overlap matrices, respectively (see Appendix A):

$$F_{\mu\mu'}(\boldsymbol{k}) = \sum_{\boldsymbol{m}} e^{i\boldsymbol{k}\cdot\boldsymbol{m}} F_{\mu\boldsymbol{0},\mu'\boldsymbol{m}}, \tag{12a}$$

$$S_{\mu\mu'}(\boldsymbol{k}) = \sum_{\boldsymbol{m}} e^{i\boldsymbol{k}\cdot\boldsymbol{m}} S_{\mu\boldsymbol{0},\mu'\boldsymbol{m}}, \tag{12b}$$

and

$$F_{\mu\mathbf{0},\mu'\mathbf{m}} = \int_{\mathbb{R}^3} \chi_{\mu\mathbf{0}}^\dagger(\mathbf{r}) \hat{F} \chi_{\mu'\mathbf{m}}(\mathbf{r}) d^3\mathbf{r}, \qquad (13\text{a})$$

$$S_{\mu\mathbf{0},\mu'\mathbf{m}} = \int_{\mathbb{R}^3} \chi_{\mu\mathbf{0}}^\dagger(\mathbf{r}) \chi_{\mu'\mathbf{m}}(\mathbf{r}) d^3\mathbf{r}. \qquad (13\text{b})$$

We have here exploited the translational invariance of the Fock operator, which allows us to consider only the reference unit cell $\mathbf{m} = \mathbf{0}$ for the bra function $\chi_{\mu\mathbf{0}}^\dagger$, and to solve Eq. (11) independently for each $\mathbf{k}$. Finally, we express the real-space integrals in Eqs. (13) utilizing Eqs. (2) and (3) to obtain the 4c matrix forms for $F_{\mu\mathbf{0},\mu'\mathbf{m}}$ and $S_{\mu\mathbf{0},\mu'\mathbf{m}}$:

$$F_{\mu\mathbf{0},\mu'\mathbf{m}} = \begin{pmatrix} \mathcal{V}^{LL} & \mathcal{T} \\ \mathcal{T} & \frac{1}{4c^2}\mathcal{V}^{SS} - \mathcal{T} \end{pmatrix}_{\mu\mathbf{0},\mu'\mathbf{m}}, \qquad (14)$$

$$S_{\mu\mathbf{0},\mu'\mathbf{m}} = \begin{pmatrix} \mathcal{S} & 0_2 \\ 0_2 & \frac{1}{2c^2}\mathcal{T} \end{pmatrix}_{\mu\mathbf{0},\mu'\mathbf{m}}, \qquad (15)$$

where the indices $\mu\mathbf{0}, \mu'\mathbf{m}$ are applied to each element of the matrices individually and

$$\mathcal{S}_{\mu\mathbf{0},\mu'\mathbf{m}} = \mathbb{I}_2 \otimes \int_{\mathbb{R}^3} g_{\mu\mathbf{0}}(\mathbf{r}) g_{\mu'\mathbf{m}}(\mathbf{r}) d^3\mathbf{r}, \qquad (16\text{a})$$

$$\mathcal{T}_{\mu\mathbf{0},\mu'\mathbf{m}} = \mathbb{I}_2 \otimes \int_{\mathbb{R}^3} g_{\mu\mathbf{0}}(\mathbf{r}) \frac{p^2}{2} g_{\mu'\mathbf{m}}(\mathbf{r}) d^3\mathbf{r}, \qquad (16\text{b})$$

$$\mathcal{V}^{LL}_{\mu\mathbf{0},\mu'\mathbf{m}} = \mathbb{I}_2 \otimes \int_{\mathbb{R}^3} g_{\mu\mathbf{0}}(\mathbf{r}) V(\mathbf{r}) g_{\mu'\mathbf{m}}(\mathbf{r}) d^3\mathbf{r}, \qquad (16\text{c})$$

$$\mathcal{V}^{SS}_{\mu\mathbf{0},\mu'\mathbf{m}} = \int_{\mathbb{R}^3} [(\boldsymbol{\sigma}\cdot\mathbf{p}) g_{\mu\mathbf{0}}(\mathbf{r})]^\dagger V(\mathbf{r}) [(\boldsymbol{\sigma}\cdot\mathbf{p}) g_{\mu'\mathbf{m}}(\mathbf{r})] d^3\mathbf{r}. \qquad (16\text{d})$$

Integrals over the GTOs in Eqs. (16) are evaluated analytically using the recurrence scheme of Obara and Saika.[92,98] If we now let

$$T = \begin{pmatrix} 0_2 & \mathcal{T} \\ \mathcal{T} & -\mathcal{T} \end{pmatrix}, \qquad V = \begin{pmatrix} \mathcal{V}^{LL} & 0_2 \\ 0_2 & \frac{1}{4c^2}\mathcal{V}^{SS} \end{pmatrix}, \qquad (17)$$

be the 4c kinetic energy matrix and the potential matrix, respectively, where we have omitted the $\mu\mathbf{0}, \mu'\mathbf{m}$ indices, the DKS Fock matrix in Eq. (14) can be partitioned as:

$$F = T + V = T + J + V^{\text{XC}}. \qquad (18)$$

Here, J is the Coulomb and V^{XC} is the exchange–correlation contribution to the potential matrix V (the evaluation of these contributions will be discussed in more detail in Sections II E and II G, respectively). The Coulomb matrix J contains both the electron-nuclear interaction and the Hartree mean-field interaction term. The exact exchange matrix required for Hartree–Fock theory or hybrid DFT is omitted in this work.

Within the framework of DFT, Eq. (11) must be solved self-consistently, since V contains the mean-field potential as well as the exchange–correlation potential, both of which depend on the electron density and its gradients and which are constructed from the COs $\psi_i(\mathbf{k};\mathbf{r})$. Eq. (11) is solved in an iterative manner: its solutions are used to build a new Fock matrix F, Eq. (11) is then solved for this updated potential until convergence is reached.

B. Density and density matrix

In this section we formulate the real-space 4c reduced one-electron density matrix $D^{\mu\mathbf{m},\mu'\mathbf{0}}$ and the electron density ρ_{e} for periodic systems that are used in practice for the construction of the Fock matrix [Eq. (14)] instead of $\psi_i(\mathbf{k};\mathbf{r})$.

The reciprocal-space density matrix expressed in terms of COs is a diagonal matrix, where the diagonal elements form an occupation vector $f_p(\mathbf{k})$ for each band p. $f_p(\mathbf{k})$ is a zero-temperature limit of the Fermi–Dirac distribution

$$f_p(\mathbf{k}) = \frac{1}{e^{\beta(\varepsilon_p(\mathbf{k})-\mu)}+1} \xrightarrow{\beta\to\infty} \vartheta(\mu - \varepsilon_p(\mathbf{k})), \qquad (19)$$

where μ is the Fermi level chemical potential, β is the inverse temperature, and ϑ is the Heaviside step function. Bands corresponding to positronic (negative-energy) states are left vacant. If we let $f(\mathbf{k})$ denote the diagonal matrix of occupation numbers, we can write the $\mathbf{k}$-space density matrix in its block-diagonal form as

$$D(\mathbf{k},\mathbf{k}') = \delta(\mathbf{k}-\mathbf{k}')D(\mathbf{k}), \qquad (20)$$

$$D(\mathbf{k}) = c(\mathbf{k})f(\mathbf{k})c^\dagger(\mathbf{k}), \qquad (21)$$

where δ is the Dirac delta function. Inverting the Fourier series in Eq. (6), gives

$$\chi_{\mu\mathbf{m}}(\mathbf{r}) = \frac{1}{\sqrt{|\mathcal{K}|}} \int_{\mathcal{K}} e^{-i\mathbf{k}\cdot\mathbf{m}} \varphi_\mu(\mathbf{k};\mathbf{r}) d^3\mathbf{k}, \qquad (22)$$

which we use together with Eq. (20) to obtain the real-space density matrix as a quadrature

$$D^{\mu\mathbf{m},\mu'\mathbf{m}'} = \frac{1}{|\mathcal{K}|} \int_{\mathcal{K}} e^{i\mathbf{k}\cdot(\mathbf{m}-\mathbf{m}')} D^{\mu\mu'}(\mathbf{k}) d^3\mathbf{k},$$

where $D^{\mu\mu'}(\mathbf{k})$ are elements of the matrix defined in Eq. (21). In practice, it is enough to restrict ourselves only to nonequivalent elements (see Appendix A):

$$D^{\mu\mathbf{m},\mu'\mathbf{0}} = \frac{1}{|\mathcal{K}|} \int_{\mathcal{K}} e^{i\mathbf{k}\cdot\mathbf{m}} D^{\mu\mu'}(\mathbf{k}) d^3\mathbf{k}. \qquad (23)$$

The electron charge density can be evaluated as (the minus sign is for the electron charge)

$$\rho_{\text{e}}(\mathbf{r}) \equiv -\sum_p \int_{\mathcal{K}} \text{Tr}\left[\psi_p(\mathbf{k};\mathbf{r})\psi_p^\dagger(\mathbf{k};\mathbf{r})f_p(\mathbf{k})\right] d^3\mathbf{k}, \qquad (24)$$

where the trace (Tr) indicates a sum of diagonal elements of the resulting 4×4 matrix. Equivalently, we can write

$$\rho_{\text{e}}(\mathbf{r}) = -\int_{\mathcal{K}} \text{Tr}\left[\varphi_{\mu'}(\mathbf{k};\mathbf{r})D^{\mu'\mu}(\mathbf{k})\varphi_\mu^\dagger(\mathbf{k};\mathbf{r})\right] d^3\mathbf{k}, \qquad (25)$$

$$= -\sum_{\mathbf{m}\mathbf{m}'} \text{Tr}\left[\chi_{\mu'\mathbf{m}'}(\mathbf{r})D^{\mu'\mathbf{m}',\mu\mathbf{m}}\chi_{\mu\mathbf{m}}^\dagger(\mathbf{r})\right]. \qquad (26)$$

Let us define the 4c *overlap distribution function*

$$\Omega_{\mu\boldsymbol{m},\mu'\boldsymbol{m}'}(\boldsymbol{r}) \equiv \chi_{\mu\boldsymbol{m}}^{\dagger}(\boldsymbol{r})\chi_{\mu'\boldsymbol{m}'}(\boldsymbol{r})$$
$$= \begin{pmatrix} \Omega^{LL}(\boldsymbol{r}) & 0_2 \\ 0_2 & \Omega^{SS}(\boldsymbol{r}) \end{pmatrix}_{\mu\boldsymbol{m},\mu'\boldsymbol{m}'}. \qquad (27)$$

If we use

$$\Omega_{\mu\boldsymbol{m},\mu'\boldsymbol{m}'}(\boldsymbol{r}) = \Omega_{\mu\boldsymbol{0},\mu'\boldsymbol{m}'-\boldsymbol{m}}(\boldsymbol{r}-\boldsymbol{m}), \qquad (28)$$

together with the translational invariance of the density matrix

$$D^{\mu'\boldsymbol{m}',\mu\boldsymbol{m}} = D^{\mu'\boldsymbol{m}'-\boldsymbol{m},\mu\boldsymbol{0}}, \qquad (29)$$

then the electron charge density becomes (after changing the summation variables)

$$\rho_{\rm e}(\boldsymbol{r}) = -\sum_{\boldsymbol{m}\boldsymbol{n}} {\rm Tr}\left[\Omega_{\mu\boldsymbol{0},\mu'\boldsymbol{m}}(\boldsymbol{r}-\boldsymbol{n})D^{\mu'\boldsymbol{m},\mu\boldsymbol{0}}\right]. \qquad (30)$$

We now collect indices $\mu\boldsymbol{0},\mu'\boldsymbol{m} \equiv u$ and $\mu'\boldsymbol{m},\mu\boldsymbol{0} \equiv \bar{u}$, and introduce a shorthand notation for the trace in real space for an arbitrary operator A

$$A_u D^{\bar{u}} \equiv \sum_{\boldsymbol{m}} A_{\mu\boldsymbol{0},\mu'\boldsymbol{m}}D^{\mu'\boldsymbol{m},\mu\boldsymbol{0}}. \qquad (31)$$

We can then express the total charge density as a sum of nuclear and electronic contributions

$$\rho(\boldsymbol{r}) = \sum_{\boldsymbol{n}} \tilde{\rho}(\boldsymbol{r}-\boldsymbol{n}), \qquad (32)$$

$$\tilde{\rho}(\boldsymbol{r}) = \tilde{\rho}_{\rm n}(\boldsymbol{r}) + \tilde{\rho}_{\rm e}(\boldsymbol{r}), \qquad (33)$$

obtained from the *auxiliary* densities $\tilde{\rho}_{\rm n}$ and $\tilde{\rho}_{\rm e}$ translated from the reference unit cell to the cell $\boldsymbol{n}$. The auxiliary densities for the reference unit cell are defined as

$$\tilde{\rho}_{\rm n}(\boldsymbol{r}) \equiv \sum_{A} Z_A \delta(\boldsymbol{r}-\boldsymbol{A}), \qquad (34a)$$

$$\tilde{\rho}_{\rm e}(\boldsymbol{r}) \equiv -{\rm Tr}\left[\Omega_u(\boldsymbol{r})D^{\bar{u}}\right], \qquad (34b)$$

where A labels atoms in the reference unit cells, Z_A and $\boldsymbol{A}$ being their charge and position, respectively. Let

$$N = \sum_{\boldsymbol{n}} 1 \qquad (35)$$

be the infinite number of unit cells in a crystal and $N_{\rm e}$ the number of electrons per unit cell. The electron charge density $\rho_{\rm e}$ must integrate to minus the total (infinite) number of electrons, *i.e.*

$$\int_{\mathbb{R}^3} \rho_{\rm e}(\boldsymbol{r})d^3\boldsymbol{r} = -N N_{\rm e}. \qquad (36)$$

Hence, we can infer from Eq. (32) that the auxiliary electron density $\tilde{\rho}_{\rm e}$ integrates to minus the number of electrons per unit cell $N_{\rm e}$. Moreover, integration of Eq. (34b) gives

$$ {\rm Tr}\left(S_u D^{\bar{u}}\right) = N_{\rm e}, \qquad (37)$$

where $S_u \equiv S_{\mu\boldsymbol{0},\mu'\boldsymbol{m}}$ is the 4c overlap matrix from Eq. (15). Note, however, that whereas the total electron density $\rho_{\rm e}$ is a periodic function with the lattice periodicity, the auxiliary density $\tilde{\rho}_{\rm e}$ is not periodic. Nuclear charge densities follow the same arguments. In addition, partitioning the total density in Eqs. (32) and (33) into contributions from individual unit cells ensures that the lattice sum over $\boldsymbol{n}$ is performed in a charge-neutral manner,[99,100] *i.e.*

$$\forall \boldsymbol{n}: \quad \int_{\mathbb{R}^3} \tilde{\rho}(\boldsymbol{r}-\boldsymbol{n})d^3\boldsymbol{r} = 0, \qquad (38)$$

provided that there is no excess of positive or negative charge in a unit cell.

C. Time reversal symmetry

In the present work, we solve the DKS equation in $\boldsymbol{k}$-space [Eq. (11)] by exploiting the time reversal (TR) symmetry of the Fock operator. In the absence of a vector potential and in non-magnetic systems, TR-symmetric operators attain a special structure in the so-called *Kramers-restricted* basis.[101–104] This allows us to reduce the computational and memory resources needed in a calculation and it also facilitates the interpretation of band structures. Here we will generalize the concept of a Kramers-restricted GTO basis to reciprocal space, and explicitly show the structure of the TR-symmetric operators expressed in this basis.

We start by briefly reviewing the TR operator, which is an antilinear one-electron operator defined in the 4c realm as[102,104,105]

$$\mathcal{K} = -i\begin{pmatrix} \sigma_y & 0_2 \\ 0_2 & \sigma_y \end{pmatrix}\mathcal{K}_0, \qquad (39)$$

where $\mathcal{K}_0$ denotes complex conjugation. The TR operator satisfies $\mathcal{K}^{\dagger} = -\mathcal{K}$ and $\mathcal{K}^{\dagger}\mathcal{K} = \mathbb{I}_4$. An operator $\hat{A}$ is *time-reversal symmetric* iff it commutes with $\mathcal{K}$ ($[\cdot,\cdot]$ denotes a commutator):

$$\left[\hat{A},\mathcal{K}\right] = 0. \qquad (40)$$

Let us express the TR-symmetric operator $\hat{A}$ in the Kramers-restricted basis $\{|p\rangle, |\bar{p}\rangle\}$, where $|\bar{p}\rangle \equiv \mathcal{K}|p\rangle$ denotes the Kramers partner of $|p\rangle$. If $a \equiv \langle p|\hat{A}|p\rangle$ and $b \equiv \langle p|\hat{A}|\bar{p}\rangle$ label two distinct elements of A, then the remaining 2 elements are given by

$$\langle \bar{p}|\hat{A}|p\rangle = \langle \mathcal{K}p|\hat{A}^{\dagger}|p\rangle = \langle p|\mathcal{K}^{\dagger}\hat{A}|p\rangle^{*} =$$
$$= -\langle p|\mathcal{K}\hat{A}|p\rangle^{*} = -\langle p|\hat{A}\mathcal{K}|p\rangle^{*} = -b^{*}$$

and

$$\langle \bar{p}|\hat{A}|\bar{p}\rangle = \langle p|\mathcal{K}^{\dagger}\hat{A}\mathcal{K}|p\rangle^{*} = \langle p|\hat{A}\mathcal{K}^{\dagger}\mathcal{K}|p\rangle^{*} =$$
$$= \langle p|\hat{A}|p\rangle^{*} = a^{*}.$$

Hence the matrix representation of the operator $\hat{A}$ has the following TR-symmetric structure:

$$A = \begin{pmatrix} a & b \\ -b^* & a^* \end{pmatrix}. \tag{41}$$

Note, that the Hermitian adjoint of an antilinear operator involves complex conjugation of the inner product.

The RKB basis defined in Eq. (2) is Kramers-restricted in real space, and can be written as[102,103]

$$\chi_\mu(\boldsymbol{r}) = \begin{pmatrix} a & b \\ -b^* & a^* \end{pmatrix} g_\mu(\boldsymbol{r}), \tag{42}$$

where

$$a \equiv \begin{pmatrix} 1 & 0 \\ 0 & \frac{\nabla_z}{2ic} \end{pmatrix}, \qquad b \equiv \begin{pmatrix} 0 & 0 \\ 0 & \frac{\nabla_x}{2ic} - \frac{\nabla_y}{2c} \end{pmatrix}, \tag{43}$$

where we rearranged the 4×4 matrix to emphasize the TR-symmetric structure of the basis. Using the transformation in Eq. (6), we obtain the 4c Kramers-restricted Bloch functions that constitute our basis in $\boldsymbol{k}$-space, and which acquire the structure

$$\varphi_\mu(\boldsymbol{k}; \boldsymbol{r}) = \begin{pmatrix} a(\boldsymbol{k}; \boldsymbol{r}) & b(\boldsymbol{k}; \boldsymbol{r}) \\ -b^*(-\boldsymbol{k}; \boldsymbol{r}) & a^*(-\boldsymbol{k}; \boldsymbol{r}) \end{pmatrix}_\mu, \tag{44}$$

where

$$a(\boldsymbol{k}; \boldsymbol{r}) = \frac{1}{\sqrt{|\mathcal{K}|}} \sum_{\boldsymbol{m}} e^{i\boldsymbol{k}\cdot\boldsymbol{m}} a \, g_\mu(\boldsymbol{r} - \boldsymbol{m}), \tag{45a}$$

$$b(\boldsymbol{k}; \boldsymbol{r}) = \frac{1}{\sqrt{|\mathcal{K}|}} \sum_{\boldsymbol{m}} e^{i\boldsymbol{k}\cdot\boldsymbol{m}} b \, g_\mu(\boldsymbol{r} - \boldsymbol{m}). \tag{45b}$$

As a consequence of the Kramers-restricted basis, the TR-symmetric operator $\hat{A}$ takes the matrix form of

$$A_{\mu\boldsymbol{0},\mu'\boldsymbol{m}} = \begin{pmatrix} a & b \\ -b^* & a^* \end{pmatrix}_{\mu\boldsymbol{0},\mu'\boldsymbol{m}}, \tag{46}$$

in real space, and after the transformation to $\boldsymbol{k}$-space [Eqs. (12)], we have

$$A_{\mu\mu'}(\boldsymbol{k}) = \begin{pmatrix} a(\boldsymbol{k}) & b(\boldsymbol{k}) \\ -b^*(-\boldsymbol{k}) & a^*(-\boldsymbol{k}) \end{pmatrix}_{\mu\mu'}, \tag{47}$$

where $a_{\mu\mu'}(\boldsymbol{k}) = \sum_{\boldsymbol{m}} e^{i\boldsymbol{k}\cdot\boldsymbol{m}} a_{\mu\boldsymbol{0},\mu'\boldsymbol{m}}$ (and likewise for b).

We now prove two important corollaries of the TR symmetry in our scheme, namely: 1) that the band energies have a $\boldsymbol{k}$-inversion symmetry (as in the nonrelativistic case); and 2) that the density matrix inherits the TR structure from the Fock matrix. In addition, it can be shown that a new Fock matrix constructed from the TR-symmetric density matrix is also TR-symmetric. This implies that the TR structure is persevered in the self-consistent procedure, allowing us to impose this structure in the algorithm, significantly reducing computational and memory demands in the calculations. Let us

assume the TR structure in Eq. (47) for the Fock matrix $F(\boldsymbol{k})$, and apply $\mathcal{K}$ from the left to the eigenvalue problem in Eq. (11)

$$\mathcal{K}F(\boldsymbol{k})c(\boldsymbol{k}) = \mathcal{K}S(\boldsymbol{k})c(\boldsymbol{k})\varepsilon(\boldsymbol{k}). \tag{48}$$

Since $\mathcal{K}$ commutes with the real-space Fock matrix, and trivially also with the overlap matrix $S(\boldsymbol{k})$, it follows that

$$\mathcal{K}F(\boldsymbol{k}) = F(-\boldsymbol{k})\mathcal{K}, \tag{49a}$$

$$\mathcal{K}S(\boldsymbol{k}) = S(-\boldsymbol{k})\mathcal{K}. \tag{49b}$$

Flipping $\boldsymbol{k} \to -\boldsymbol{k}$ in Eq. 48 gives

$$F(\boldsymbol{k})\mathcal{K}c(-\boldsymbol{k}) = S(\boldsymbol{k})\mathcal{K}c(-\boldsymbol{k})\varepsilon(-\boldsymbol{k}). \tag{50}$$

Because the energies $\varepsilon(\boldsymbol{k})$ are real, we can infer that $\{c(\boldsymbol{k}), \mathcal{K}c(-\boldsymbol{k})\}$ both are solutions of the eigenvalue equation Eq. (11) with energies $\{\varepsilon(\boldsymbol{k}), \varepsilon(-\boldsymbol{k})\}$, and thus form a Kramers pair. Let us introduce the following notation for the Kramers partners:

$$\bar{c}(\boldsymbol{k}) = \mathcal{K}c(-\boldsymbol{k}), \tag{51a}$$

$$\bar{\varepsilon}(\boldsymbol{k}) = \varepsilon(-\boldsymbol{k}), \tag{51b}$$

$$\bar{f}(\boldsymbol{k}) = f(-\boldsymbol{k}), \tag{51c}$$

where the last equation follows from Eq. (19). In addition, Eqs. (51) imply that the density matrix in reciprocal space has the TR-symmetric structure of Eq. (47). To prove this, we use the block-diagonal structure of the operator $\mathcal{K}$, and without loss of generality we restrict ourselves to a 2×2 Fock matrix with solutions

$$c(\boldsymbol{k}) = \begin{pmatrix} c^{\mathrm{u}}(\boldsymbol{k}) & \bar{c}^{\mathrm{u}}(\boldsymbol{k}) \\ c^{\mathrm{l}}(\boldsymbol{k}) & \bar{c}^{\mathrm{l}}(\boldsymbol{k}) \end{pmatrix}, \tag{52}$$

where u and l denote the upper and lower spinor components, respectively. The second column is related to the first via the TR operation Eq. (51a), thus $\bar{c}^{\mathrm{u}}(\boldsymbol{k}) = -c^{\mathrm{l}*}(-\boldsymbol{k})$ and $\bar{c}^{\mathrm{l}}(\boldsymbol{k}) = c^{\mathrm{u}*}(-\boldsymbol{k})$. The density matrix element D^{lu} then satisfies

$$\begin{aligned} D^{\mathrm{lu}}(\boldsymbol{k}) &= c^{\mathrm{l}}(\boldsymbol{k})f(\boldsymbol{k})c^{\mathrm{u}*}(\boldsymbol{k}) + \bar{c}^{\mathrm{l}}(\boldsymbol{k})\bar{f}(\boldsymbol{k})\bar{c}^{\mathrm{u}*}(\boldsymbol{k}) \\ &= -\bar{c}^{\mathrm{u}*}(-\boldsymbol{k})\bar{f}(-\boldsymbol{k})\bar{c}^{\mathrm{l}}(-\boldsymbol{k}) \\ &\quad - c^{\mathrm{u}*}(-\boldsymbol{k})f(-\boldsymbol{k})c^{\mathrm{l}}(-\boldsymbol{k}) \\ &= -D^{\mathrm{ul}*}(-\boldsymbol{k}). \end{aligned}$$

Similarly $D^{\mathrm{ll}}(\boldsymbol{k}) = D^{uu*}(-\boldsymbol{k})$. It follows that the real-space elements of the density matrix obtained from Eq. (23) have the TR structure in Eq. (46).

D. Quaternion operators

Owing to the specific structure of TR-symmetric operators, a compact notation which leads to a very efficient computer implementation can be achieved with the use

of quaternion algebra (or its isomorphisms).[86,87,102,103] This formulation identifies the integrals that are non-redundant and non-zero when constructing operators in the RKB basis Eq. (2), and allows us to formulate an efficient relativistic algorithm to solve the DKS equation. Let $\mathrm{Re}\,x$ and $\mathrm{Im}\,x$ denote the real and imaginary parts of a complex number x, respectively. Then a TR-symmetric matrix A is written as

$$A = \begin{pmatrix} a & b \\ -b^* & a^* \end{pmatrix} = \sum_{q=0}^{3} A^q e_q \equiv A^q e_q, \qquad (53)$$

where

$$A^0 = \mathrm{Re}\,a \qquad\quad e_0 = \mathbb{I}_2 \equiv 1, \qquad (54a)$$

$$A^1 = \mathrm{Im}\,a \qquad\quad e_1 = i\sigma_z \equiv \breve{i}, \qquad (54b)$$

$$A^2 = \mathrm{Re}\,b \qquad\quad e_2 = i\sigma_y \equiv \breve{j}, \qquad (54c)$$

$$A^3 = \mathrm{Im}\,b \qquad\quad e_3 = i\sigma_x \equiv \breve{k}, \qquad (54d)$$

and $\breve{i}, \breve{j}, \breve{k}$ are fundamental quaternion units obeying

$$\breve{i}^2 = \breve{j}^2 = \breve{k}^2 = \breve{i}\breve{j}\breve{k} = -1. \qquad (55)$$

The Hermitian conjugation of A changes the sign of the three imaginary components, so that

$$A^\dagger = (A^0 e_0 + A^1 e_1 + A^2 e_2 + A^3 e_3)^\dagger$$
$$= A^{0,T} e_0 - A^{1,T} e_1 - A^{2,T} e_2 - A^{3,T} e_3, \qquad (56)$$

where $A^{q,T}$ denotes the transpose of the real matrix A^q. We decompose the TR-symmetric matrices according to Eq. (53) and refer to A^q as quaternion components regardless of whether e_q are interpreted as matrices or quaternion units. All algebraic manipulations can be performed in an equivalent manner in both algebras, and it is only a matter of personal preference to select a suitable representation. However, we emphasize that encoding complex 4c TR-symmetric matrices using four real A^q components reduces the number of non-zero terms by a factor of two, and often reveals important structures of the operators, facilitating further reductions.[87]

Matrix elements of a 4c TR-symmetric operator $\hat{A}$ in the basis defined in Eqs. (42) and (4) are expressed in real space as

$$A_{\mu\mathbf{0},\mu'\mathbf{m}} = A^q_{\mu\mathbf{0},\mu'\mathbf{m}} e_q, \qquad (57)$$

where $A^q_{\mu\mathbf{0},\mu'\mathbf{m}}$ are 2×2 real matrices:

$$A^q_{\mu\mathbf{0},\mu'\mathbf{m}} = \begin{pmatrix} A^{LL,q} & A^{LS,q} \\ A^{SL,q} & A^{SS,q} \end{pmatrix}_{\mu\mathbf{0},\mu'\mathbf{m}}. \qquad (58)$$

Reciprocal-space quaternion components of A are defined by the Fourier series

$$A^q_{\mu\mu'}(\mathbf{k}) = \sum_{\mathbf{m}} e^{i\mathbf{k}\cdot\mathbf{m}} A^q_{\mu\mathbf{0},\mu'\mathbf{m}}, \qquad (59)$$

and form a quaternion (dropping the $\mu\mu'$ indices)

$$A(\mathbf{k}) = A^q(\mathbf{k}) e_q, \qquad (60)$$

with complex-valued components $A^q(\mathbf{k})$.

During the self-consistent procedure, we exchange the quaternion form of the Fock matrix with its complex form Eq. (47), and vice versa. Whereas the quaternion form is more beneficial in real space to facilitate the integral evaluation when assembling the Fock matrix, the matrix form is inevitable in the diagonalization step of the procedure. Additionally, if we establish a direct connection between these forms in reciprocal space, we avoid unnecessary computations of the Fourier series, because there are considerably fewer nonzero quaternion components than complex matrix elements. Therefore, we use the definitions in Eqs. (54) together with Eq. (60) to compose a complex matrix

$$A(\mathbf{k}) \equiv \begin{pmatrix} A^0(\mathbf{k}) + iA^1(\mathbf{k}) & A^2(\mathbf{k}) + iA^3(\mathbf{k}) \\ -A^2(\mathbf{k}) + iA^3(\mathbf{k}) & A^0(\mathbf{k}) - iA^1(\mathbf{k}) \end{pmatrix}. \qquad (61)$$

This matrix is consistent with Eq. (47), because the definition of the reciprocal-space quaternion components [Eq. (59)] implies

$$A^{q*}(\mathbf{k}) = A^q(-\mathbf{k}). \qquad (62)$$

Inverting this process allows us to map a complex matrix

$$A(\mathbf{k}) = \begin{pmatrix} a(\mathbf{k}) & b(\mathbf{k}) \\ c(\mathbf{k}) & d(\mathbf{k}) \end{pmatrix}$$

with assumed TR symmetry [$c(\mathbf{k}) = -b^*(-\mathbf{k})$, $d(\mathbf{k}) = a^*(-\mathbf{k})$] to a complex quaternion with components given by

$$A^0(\mathbf{k}) = \frac{1}{2}\left[a(\mathbf{k}) + d(\mathbf{k})\right], \qquad (63a)$$

$$A^1(\mathbf{k}) = \frac{1}{2i}\left[a(\mathbf{k}) - d(\mathbf{k})\right], \qquad (63b)$$

$$A^2(\mathbf{k}) = \frac{1}{2}\left[b(\mathbf{k}) - c(\mathbf{k})\right], \qquad (63c)$$

$$A^3(\mathbf{k}) = \frac{1}{2i}\left[b(\mathbf{k}) + c(\mathbf{k})\right]. \qquad (63d)$$

For $\mathbf{k} = \mathbf{0}$ quaternion components $A^q(\mathbf{0})$ are real, and Eqs. (63) coincide with the definitions in Eqs. (54).

We now rewrite all operators in Eqs. (16) that enter the DKS equation in the language of quaternions. Scalar operators $\mathcal{S}, \mathcal{T}$, and $\mathcal{V}^{LL}$ have a trivial structure in the spin space, therefore their corresponding quaternions have nonzero real part (0-th component) and zero imaginary part. On the other hand, the operator $\mathcal{V}^{SS}$ contains Pauli matrices, and thus is a general quaternion $\mathcal{V}^{SS} = \mathcal{V}^{SS,q} e_q$. The Fock matrix in Eq. (14) can then be expressed as (omitting $\mu\mathbf{0}, \mu'\mathbf{m}$ indices for clarity)

$$F = \begin{pmatrix} \mathcal{V}^{LL,0} & \mathcal{T}^0 \\ \mathcal{T}^0 & \frac{1}{4c^2}\mathcal{V}^{SS,0} - \mathcal{T}^0 \end{pmatrix} e_0 + \begin{pmatrix} 0 & 0 \\ 0 & \frac{1}{4c^2}\mathcal{V}^{SS,i} \end{pmatrix} e_i, \qquad (64)$$

for $i = 1, 2, 3$. It is convenient to rewrite the potential V in terms of the 4c overlap distribution Ω defined in Eq. (27). We accomplish this by rewriting Eq. (16d) as

$$\mathcal{V}^{SS}_{\mu\mathbf{0},\mu'\boldsymbol{m}} = \int_{\mathbb{R}^3} [(\boldsymbol{\sigma} \cdot \boldsymbol{p})g_{\mu\mathbf{0}}(\boldsymbol{r})]^\dagger [(\boldsymbol{\sigma} \cdot \boldsymbol{p})g_{\mu'\boldsymbol{m}}(\boldsymbol{r})] V(\boldsymbol{r})d^3\boldsymbol{r}.$$

The small-component overlap distribution is a product of small-component basis functions [Eq. (3b)], so

$$\Omega^{SS}_{\mu\mathbf{0},\mu'\boldsymbol{m}} = \frac{1}{4c^2} [(\boldsymbol{\sigma} \cdot \boldsymbol{p})g_{\mu\mathbf{0}}]^\dagger [(\boldsymbol{\sigma} \cdot \boldsymbol{p})g_{\mu'\boldsymbol{m}}]. \tag{65}$$

The potential therefore becomes

$$\mathcal{V}^{LL}_u = \int_{\mathbb{R}^3} \Omega^{LL}_u(\boldsymbol{r})V(\boldsymbol{r})d^3\boldsymbol{r}, \tag{66a}$$

$$\frac{1}{4c^2}\mathcal{V}^{SS}_u = \int_{\mathbb{R}^3} \Omega^{SS}_u(\boldsymbol{r})V(\boldsymbol{r})d^3\boldsymbol{r}, \tag{66b}$$

where $u \equiv \mu\mathbf{0}, \mu'\boldsymbol{m}$, and the overlap distributions are quaternions

$$\Omega^{LL}_u(\boldsymbol{r}) = \Omega^{LL,0}_u(\boldsymbol{r})e_0, \tag{67a}$$

$$\Omega^{SS}_u(\boldsymbol{r}) = \Omega^{SS,q}_u(\boldsymbol{r})e_q. \tag{67b}$$

Explicit forms of the quaternion components of Ω^{SS} can be identified if we apply the multiplication rule for the Pauli matrices to Eq. (65), *i.e.*

$$\begin{aligned}\Omega^{SS}_{\mu\mathbf{0},\mu'\boldsymbol{m}} &= \frac{1}{4c^2} (\boldsymbol{\nabla}g_{\mu\mathbf{0}})^\dagger \cdot (\boldsymbol{\nabla}g_{\mu'\boldsymbol{m}}) \, \mathbb{I}_2 \\ &+ \frac{1}{4c^2} (\boldsymbol{\nabla}g_{\mu\mathbf{0}})^\dagger \times (\boldsymbol{\nabla}g_{\mu'\boldsymbol{m}}) \cdot i\boldsymbol{\sigma}.\end{aligned} \tag{68}$$

This analysis shows that in order to build 4c complex matrices for the Coulomb and exchange–correlation operators, it is sufficient to evaluate integrals in Eqs. (66) for 5 components of the overlap distribution – one for the LL sector, and 4 for the SS sector. The $\boldsymbol{k}$-space matrix is then obtained by computing the Fourier series of these 5 components [Eq. (59)] and arranging them according to Eq. (61). Moreover, one can obtain a spin-free form of the DKS equation in solids by omitting the imaginary quaternion terms that are associated with the spin–orbit interaction, in analogy to the procedure proposed by Dyall for molecules.[106]

We conclude this section by employing the quaternion formalism to express expectation values (traces with the density matrix) of TR-symmetric operators appearing in the DKS equation. Suppose a matrix A has the same structure as the potential V, *i.e.* does not couple the large and small components of the wave function, and its LL quaternion has zero imaginary part. Its trace with a density matrix D, as defined in Eq. (31), is obtained by using the traceless property of the Pauli matrices as

$$\begin{aligned}\text{Tr}\left[A_u D^{\bar{u}}\right] &= \text{Tr}\left[\begin{pmatrix} A^{LL} & 0_2 \\ 0_2 & A^{SS} \end{pmatrix}_u \begin{pmatrix} D_{LL} & D_{LS} \\ D_{SL} & D_{SS} \end{pmatrix}^{\bar{u}}\right] \\ &= 2\left(A^{LL,0}_u D^{\bar{u}}_{LL,0} + A^{SS,0}_u D^{\bar{u}}_{SS,0} \right. \\ &\left. - A^{SS,i}_u D^{\bar{u}}_{SS,i}\right),\end{aligned} \tag{69}$$

implicitly summing over u and $i = 1, 2, 3$. Note that despite the general TR-symmetric structure of the density matrix, only its corresponding 5 elements are required to evaluate the trace. Eq. (69) also holds for the electron density in Eq. (34b) when substituting $A_u \to \Omega_u(\boldsymbol{r})$. The kinetic energy operator T [Eq. (17)] has a different structure than the potential V. We evaluate its trace with the density matrix to compute the kinetic energy per unit cell as

$$\frac{E_\text{k}}{N} = \text{Tr}\left[T_u D^{\bar{u}}\right] = \text{Tr}\left[\begin{pmatrix} 0_2 & \mathcal{T} \\ \mathcal{T} & -\mathcal{T} \end{pmatrix}_u \begin{pmatrix} D_{LL} & D_{LS} \\ D_{SL} & D_{SS} \end{pmatrix}^{\bar{u}}\right].$$

It follows that

$$\frac{E_\text{k}}{N} = 2\mathcal{T}^0_u \left(D^{\bar{u}}_{SL,0} + D^{\bar{u}}_{LS,0} - D^{\bar{u}}_{SS,0}\right). \tag{70}$$

E. Coulomb potential and energy

Using the auxiliary charge density $\tilde{\rho}$ from Eq. (32), we can express the Coulomb contribution J to the Fock matrix in Eq. (18)

$$J(\boldsymbol{r}) = -\int_{\mathbb{R}^3} \frac{\rho(\boldsymbol{r}')d^3\boldsymbol{r}'}{|\boldsymbol{r} - \boldsymbol{r}'|}, \tag{71}$$

as

$$J(\boldsymbol{r}) = -\sum_{\boldsymbol{n}} \int_{\mathbb{R}^3} \frac{\tilde{\rho}(\boldsymbol{r}')d^3\boldsymbol{r}'}{|\boldsymbol{r} - \boldsymbol{r}' - \boldsymbol{n}|}. \tag{72}$$

We see that the Coulomb potential is a periodic function with the lattice periodicity, given that the lattice sum over $\boldsymbol{n}$ runs over the entire infinite lattice. Any truncation of this sum (for instance, for numerical purposes) will violate the translational symmetry. We express the non-equivalent matrix elements of J in the real-space basis defined in Eqs. (4) and (2) as

$$J_{\mu\mathbf{0},\mu'\boldsymbol{m}} = \int_{\mathbb{R}^3} \chi^\dagger_{\mu\mathbf{0}}(\boldsymbol{r})J(\boldsymbol{r})\chi_{\mu'\boldsymbol{m}}(\boldsymbol{r})d^3\boldsymbol{r}.$$

Since the Coulomb potential $J(\boldsymbol{r})$ is diagonal in the 4×4 bispinor space, it follows that

$$\begin{aligned}J_u &= \int_{\mathbb{R}^3} \Omega_u(\boldsymbol{r})J(\boldsymbol{r})d^3\boldsymbol{r} \\ &= -\sum_{\boldsymbol{n}} \int_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\Omega_u(\boldsymbol{r}_1)\tilde{\rho}(\boldsymbol{r}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2 - \boldsymbol{n}|}d^3\boldsymbol{r}_1 d^3\boldsymbol{r}_2,\end{aligned} \tag{73}$$

where $u \equiv \mu\mathbf{0}, \mu'\boldsymbol{m}$, and Ω is the 4c overlap distribution defined in Eqs. (27) and (67). Substituting the nuclear and electronic auxiliary densities [Eqs. (34)], we obtain

$$J_u = \sum_{\boldsymbol{n}} \left[J^\text{n}_u(\boldsymbol{n}) + J^\text{e}_u(\boldsymbol{n})\right], \tag{74a}$$

$$J^\text{n}_u(\boldsymbol{n}) = \sum_A \int_{\mathbb{R}^3} \frac{-Z_A\Omega_u(\boldsymbol{r})}{|\boldsymbol{r} - \boldsymbol{A} - \boldsymbol{n}|}d^3\boldsymbol{r}, \tag{74b}$$

$$J^\text{e}_u(\boldsymbol{n}) = \int_{\mathbb{R}^3\times\mathbb{R}^3} \frac{\Omega_u(\boldsymbol{r}_1) \text{Tr}\left[\Omega_v(\boldsymbol{r}_2)D^{\bar{v}}\right]}{|\boldsymbol{r}_1 - \boldsymbol{r}_2 - \boldsymbol{n}|}d^3\boldsymbol{r}_1 d^3\boldsymbol{r}_2. \tag{74c}$$

Note that in Eq. (74c), the sum over $v \equiv \nu\mathbf{0}, \nu'\mathbf{n}'$ is implied. This sum over v together with the lattice sum over $\mathbf{n}$ in Eq. (74a) must be computed for each $u \equiv \mu\mathbf{0}, \mu'\mathbf{m}$, making this term the most computationally expensive to evaluate.

The expression for the Coulomb energy in a periodic system can be obtained in a similar manner. Inserting the auxiliary density to

$$E_{\mathrm{C}} = \frac{1}{2} \int_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3\mathbf{r}_1 d^3\mathbf{r}_2, \qquad (75)$$

gives

$$\frac{E_{\mathrm{C}}}{N} = \frac{1}{2} \sum_{\mathbf{n}} \int_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\tilde{\rho}(\mathbf{r}_1)\tilde{\rho}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2 - \mathbf{n}|} d^3\mathbf{r}_1 d^3\mathbf{r}_2. \qquad (76)$$

If we divide the density into nuclear and electron contributions, and use the definitions in Eqs. (74b) and (74c), we obtain

$$\frac{E_{\mathrm{C}}}{N} = \frac{1}{2} \sum_{\mathbf{n}} E_{\mathrm{nn}}(\mathbf{n}) + 2\,\mathrm{Tr}\left[J_u^{\mathrm{n}}(\mathbf{n})D^{\bar{u}}\right] + \mathrm{Tr}\left[J_u^{\mathrm{e}}(\mathbf{n})D^{\bar{u}}\right], \qquad (77)$$

where

$$E_{\mathrm{nn}}(\mathbf{n}) = \overline{\sum_{AB}} \frac{Z_A Z_B}{|\mathbf{A} - \mathbf{B} - \mathbf{n}|} \qquad (78)$$

is the nuclear–nuclear repulsion energy, and the bar over the sum indicates that the divergent self-interaction terms are excluded. The traces of the 4c matrices $J_u^{\mathrm{n}}(\mathbf{n})$ and $J_u^{\mathrm{e}}(\mathbf{n})$ with the density matrix are evaluated using Eq. (69). In Eq. (77) we grouped the electron–nuclear and nuclear–electron terms together — this is only possible if $\sum_{\mathbf{n}} J_u^{\mathrm{n}}(-\mathbf{n}) = \sum_{\mathbf{n}} J_u^{\mathrm{n}}(\mathbf{n})$, so the lattice sum must contain both the $\mathbf{n}$ and $-\mathbf{n}$ unit cells for each $\mathbf{n}$. This is true for the infinite lattice sum, but should be taken into account when designing approximations to the lattice sum.

F. Treatment of electrostatic lattice sums

A complication that emerges when studying periodic systems is the evaluation of the electrostatic lattice sums $\sum_{\mathbf{n}}$ that appear in the Coulomb potential [Eq. (74a)] and the Coulomb energy [Eq. (77)]. The difficulty originates in the long-range nature of the electrostatic Coulomb interaction, and manifests itself in two ways. One issue is the question of the convergence itself. The lattice sums of individual electronic and nuclear contributions to the potential and energy are divergent, hence they must be treated in a charge-neutral manner, such as in Eqs. (74a) and (77). Assuming that the unit cell is electrically neutral, the charge-neutral lattice sums are convergent. Unfortunately, their convergence is often only conditional, and therefore the result is not determined uniquely unless physical arguments are incorporated. In such cases,

the results can be shown to depend both on the choice of the unit cell shape,[107] as well as on the implemented summation technique.[108] The convergence problems were rigorously investigated by de Leeuw *et al.*,[109] who introduced convergence factors to enforce absolute converge on the lattice sums. The second complication is the very slow convergence of the sums. Even if the sum is absolutely convergent, imprudent truncation of the sums severely distorts the potential and breaks its translational invariance. To enable the evaluation of the electrostatic potential and energy, the Coulomb operator is expanded in a spherical multipole expansion [Eq. (B6) with $\mathbf{P} = \mathbf{0}$ and $\mathbf{Q} = \mathbf{n}$]

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2 - \mathbf{n}|} = R^T(\mathbf{r}_1)\Theta(\mathbf{n})R(\mathbf{r}_2), \qquad (79)$$

where R is the vector of scaled regular solid harmonics, and Θ is the interaction tensor, defined in the work of Watson *et al.*[110] (also see Ref. 111 and Appendix B). The Coulomb problem is then reduced to the computation of the lattice sum of the spherical interaction tensors. Nijboer and De Wette proposed a universal method for computing such lattice sums.[112] Their approach is based on an Ewald-like partitioning of the sums into terms that converge rapidly in direct space, and terms that converge rapidly in reciprocal space. In this work, we follow a scheme that employs a renormalization identity, first introduced by Berman and Greengard,[113] and then later reformulated by Kudin and Scuseria.[114] Contrary to the approach of Kudin and Scuseria, we factor out the sum of the interaction tensors $\Theta(\mathbf{n})$, as shown later in this section. Because the sum of the interaction tensors only depends on the lattice parameters, we pre-calculate it before proceeding to the solution of the DKS equations.

We now apply the spherical multipole expansion in Eq. (79) to derive expressions for the Coulomb potential and energy. First we split the infinite lattice sum over $\mathbf{n}$ in Section II E

$$\sum_{\mathbf{n}} = \sum_{\mathbf{n}\in\mathrm{NF}} + \sum_{\mathbf{n}\in\mathrm{FF}}, \qquad (80)$$

where NF is the near-field and FF is the far-field of the reference unit cell $\mathbf{n} = \mathbf{0}$. FF is constructed to contain all unit cells for which a universal multipole expansion in Eq. (79) centered in $\mathbf{n} = \mathbf{0}$ produces a globally valid approximation to the integrals in Eqs. (74). A remaining finite array of unit cells constitutes the NF. Our partitioning scheme is similar to those discussed in previous studies.[85,110,115] Inserting the multipole expansion in Eq. (79) into Eqs. (73) and (76) gives the corresponding contributions to the far-field potential and energy

$$J_u^{\mathrm{FF}} = q_u^T \Lambda Q, \qquad (81)$$

$$\frac{E_{\mathrm{C}}^{\mathrm{FF}}}{N} = \frac{1}{2} Q^T \Lambda Q. \qquad (82)$$

We have here defined the lattice sum of interaction ten-

sors

$$\Lambda_{lm,jk} \equiv \sum_{\boldsymbol{n}\in\mathrm{FF}} \Theta_{lm,jk}(\boldsymbol{n}), \qquad (83)$$

elements of the 4c electronic multipole moment operator

$$q_u^{lm} \equiv -\int_{\mathbb{R}^3} \Omega_u(\boldsymbol{r}) R^{lm}(\boldsymbol{r}) d^3\boldsymbol{r}, \qquad (84)$$

and the total multipole moments of the reference unit cell

$$Q^{lm} = \int_{\mathbb{R}^3} \tilde{\rho}(\boldsymbol{r}) R^{lm}(\boldsymbol{r}) d^3\boldsymbol{r}. \qquad (85)$$

Inserting the definition of the auxiliary density from Eqs. (33) and (34) to Eq. (85) gives a more convenient expression for the total multipole moments

$$Q^{lm} = \sum_A Z_A R^{lm}(\boldsymbol{A}) + \mathrm{Tr}\left[q_u^{lm} D^{\bar{u}}\right], \qquad (86)$$

where we implied the summation over u as defined in Eq. (31). The trace of q_u^{lm} with the density matrix is computed as in Eq. (69). Notice that the total charge $Q^{00} = 0$, because $R^{00} = 1$, $q_u^{00} = -S_u$, and $\mathrm{Tr}\left[S_u D^{\bar{u}}\right] = N_e$. Furthermore, Q^{1m} is the total (electric + nuclear) dipole moment, which is gauge origin independent. To summarize, by employing the multipole expansion we accomplished two tasks: We isolated the slow-converging lattice sum $\sum_{\boldsymbol{n}}$, facilitating its subsequent computation, and we factorized the complicated six-dimensional two-electron integrals in Eq. (74c) into a product of simpler three-dimensional one-electron integrals [Eq. (84)]. In this way we obtained a very efficient scheme to incorporate the potential generated by the infinite lattice.

Analysis of the multipole expansion reveals that the problem of the conditional convergence of the Coulomb series can be attributed to non-zero unit cell dipole and quadrupole moments.[109] In fact, the 3-dimensional lattice sums of the $\Theta_{1m,00}$ and $\Theta_{00,1k}$ elements of the interaction tensor that enter the far-field potential [Eq. (82)] are divergent. To rectify this, we introduce fictitious point charges at unit cell centers, as was done in previous studies.[99,116] For each of the three periodic dimensions $i = 1, 2, 3$, two charges $\pm z^i$ are placed at opposing walls $\pm\frac{\boldsymbol{a}_i}{2}$ for each unit cell. This procedure guarantees that the unit cell remains charge neutral. Furthermore, every unit cell wall is shared by 2 unit cells, and thus contains 2 fictitious charges with opposite signs, canceling each other. Note that this scheme is valid for arbitrary unit-cell geometries. The values z^i are determined so that they eliminate the unit cell dipole moment $\boldsymbol{\mu}$, and they are obtained by solving a linear system of equations

$$z^i \boldsymbol{a}_i = -\boldsymbol{\mu}. \qquad (87)$$

To understand how the inclusion of fictitious charges resolves the problem of the conditional convergence, let us enclose a crystal sample in a finite volume, and examine

the limit of the (finite) lattice sum over unit cells inside the volume as the volume approaches infinity. The lattice sum in the Coulomb potential and energy can be shown to contain surface-dependent terms that are linear and quadratic in the position, and hence break the periodicity of the potential.[108,117] These terms do not vanish in the limit of the infinite volume, and thus the limit gives different results for different volume shapes. The fictitious charges included as described above only cancel inside the volume, not on its surface, and serve to compensate the ambiguous linear (charge–dipole) surface terms in the potential. Quadratic (charge–quadrupole) surface terms could be eliminated similarly, but because they simply shift the potential by a constant, they are ignored in this work. Such shifts affect absolute band energies, but do not alter the total energy or the band gaps.

We conclude this section by adapting the renormalization procedure of Kudin and Scuseria[114] to the evaluation of the lattice sum in Eq. (83). Instead of a direct calculation, the sum Λ is obtained as a limit

$$\Lambda = \lim_{t\to\infty} \Lambda^t. \qquad (88)$$

Λ^t are partial sums that are computed by iterating the recurrence equation

$$\Lambda^{t+1} = \Lambda^1 + \mathcal{U}(\Lambda^t)\mathcal{W}, \qquad (89)$$

where

$$\mathcal{U}(\Lambda_{lm,jk}^t) = \frac{1}{3^{l+j+1}}\Lambda_{lm,jk}^t \qquad (90)$$

is the scaling operator, and

$$\mathcal{W} = \sum_{\mu^1\ldots\mu^d=-1}^{1} W(\mu^i \boldsymbol{a}_i) \qquad (91)$$

is a matrix consisting of a sum of translation tensors W defined in Appendix B. The recurrence scheme is initiated by

$$\Lambda^1 = \sum_{\boldsymbol{n}\in\mathrm{FF}_1} \Theta(\boldsymbol{n}) \equiv \sum_{n^1\ldots n^d\in\mathrm{FF}_1} \Theta(n^i \boldsymbol{a}_i), \qquad (92)$$

where FF_1 contains all unit cells that are in the far-field of the central reference unit cell, but are in the near-field of the supercell composed of the original near-field. To illustrate this, let the near-field supercell be a block (in crystallographic coordinates) consisting of unit cells with indices $n^i = -N_i, \ldots, N_i$ for each of the periodic dimensions $i = 1, \ldots, d$. Thus the total number of unit cells in such a block is $\prod_{i=1}^d (2N_i + 1)$. Then

$$\mathrm{FF}_1 = \left\{ (n^1\ldots n^d) \in \mathbb{Z}^d; 1 \le \max_{i=1\ldots d}\left(\frac{|n^i|-1}{N_i}\right) \le 3 \right\}. \qquad (93)$$

In contrast to a naive term-by-term summation, the recurrence formula [Eq. (89)] converges rapidly to its limit, and in practice only a few iterations are needed. We provide a formal derivation of Eq. (89) in Appendix C.

G. Exchange–correlation contribution

We here derive the exchange–correlation (XC) contribution to the Fock operator and the energy of periodic systems. We assume the non-relativistic generalized gradient approximation (GGA) for the XC energy functional.[118,119] Within the Kramers-restricted (closed shell) framework GGA-type XC functional is expressed as

$$E_{\rm XC}\left[n,\boldsymbol{\nabla}n\right] \equiv E_{\rm XC} = \int_{\mathbb{R}^3} \varepsilon_{\rm XC}(\boldsymbol{r})d^3\boldsymbol{r}, \qquad (94)$$

where $\varepsilon_{\rm XC}(\boldsymbol{r}) \equiv \varepsilon_{\rm XC}\left[n,\boldsymbol{\nabla}n\right](\boldsymbol{r})$ is the XC energy density, and $n(\boldsymbol{r})$ is the total electron probability density obtained from the electron charge density in Eq. (30) as $n(\boldsymbol{r}) \equiv -\rho_{\rm e}(\boldsymbol{r})$. For periodic systems, the integration over $\mathbb{R}^3$ can be limited to an integration over the central reference unit cell, because the electron density is a periodic function with the lattice periodicity, and consequently $\varepsilon_{\rm XC}(\boldsymbol{r} + \boldsymbol{m}) = \varepsilon_{\rm XC}(\boldsymbol{r})$. Letting $\mathcal{C}_{\boldsymbol{m}}$ denote the unit cell positioned at the lattice point $\boldsymbol{m}$, we obtain

$$E_{\rm XC} = \sum_{\boldsymbol{m}} \int_{\mathcal{C}_{\boldsymbol{m}}} \varepsilon_{\rm XC}(\boldsymbol{r})d^3\boldsymbol{r} = \sum_{\boldsymbol{m}} \int_{\mathcal{C}_{\boldsymbol{0}}} \varepsilon_{\rm XC}(\boldsymbol{r}+\boldsymbol{m})d^3\boldsymbol{r}$$
$$= \sum_{\boldsymbol{m}} \int_{\mathcal{C}_{\boldsymbol{0}}} \varepsilon_{\rm XC}(\boldsymbol{r})d^3\boldsymbol{r} = N \int_{\mathcal{C}_{\boldsymbol{0}}} \varepsilon_{\rm XC}(\boldsymbol{r})d^3\boldsymbol{r},$$

where N is the total number of unit cells. Therefore, the XC energy per unit cell is

$$\frac{E_{\rm XC}}{N} = \int_{\mathcal{C}_{\boldsymbol{0}}} \varepsilon_{\rm XC}(\boldsymbol{r})d^3\boldsymbol{r}. \qquad (95)$$

The XC functional has a complicated dependence on the electron density, and the integral in Eq. (95) must therefore be integrated numerically. Because the integrand $\varepsilon_{\rm XC}$ is a highly inhomogeneous function in real space containing cusps, a robust numerical technique is needed. In this work we follow the integration scheme developed by Towler *et al.*,[84] which is an extension of Becke's atomic partitioning method[120] to periodic systems. Towler *et al.* introduced a weight function $w_A(\boldsymbol{r})$ for each atom A in the reference unit cell, and define it for all other unit cells $\mathcal{C}_{\boldsymbol{m}}$ using translations:

$$w_{A\boldsymbol{m}}(\boldsymbol{r}) \equiv w_A(\boldsymbol{r}-\boldsymbol{m}). \qquad (96)$$

The weight functions are constructed to be normalized to unity for each point $\boldsymbol{r}$, *i.e.*

$$\sum_{A\boldsymbol{m}} w_{A\boldsymbol{m}}(\boldsymbol{r}) = 1. \qquad (97)$$

The detailed process of forming the weight functions can be found in Refs. 84 and 120. Inserting the weights into Eq. (95) gives

$$\frac{E_{\rm XC}}{N} = \int_{\mathcal{C}_{\boldsymbol{0}}} \varepsilon_{\rm XC}(\boldsymbol{r}) \sum_{A\boldsymbol{m}} w_A(\boldsymbol{r}-\boldsymbol{m})d^3\boldsymbol{r}$$
$$= \sum_{A\boldsymbol{m}} \int_{\mathcal{C}_{-\boldsymbol{m}}} \varepsilon_{\rm XC}(\boldsymbol{r})w_A(\boldsymbol{r})d^3\boldsymbol{r}.$$

It follows, that

$$\frac{E_{\rm XC}}{N} = \sum_{A} \int_{\mathbb{R}^3} \varepsilon_{\rm XC}(\boldsymbol{r})w_A(\boldsymbol{r})d^3\boldsymbol{r}. \qquad (98)$$

For a discrete set of grid points $\boldsymbol{g}$, the integral is replaced by a weighted sum

$$\frac{E_{\rm XC}}{N} \to \sum_{\boldsymbol{g}} \varepsilon_{\rm XC}(\boldsymbol{g})w(\boldsymbol{g}), \qquad (99)$$

where the sum is over an integration grid composed of the joined atomic grids and, similarly, the weights $w(\boldsymbol{g})$ contain all atomic weights $w_A(\boldsymbol{g})$.

The XC potential is defined as the functional derivative of the XC energy:

$$V^{\rm XC}(\boldsymbol{r}) = \frac{\delta E_{\rm XC}}{\delta n(\boldsymbol{r})} = \frac{\partial \varepsilon_{\rm XC}}{\partial n(\boldsymbol{r})} - \boldsymbol{\nabla} \cdot \frac{\partial \varepsilon_{\rm XC}}{\partial \boldsymbol{\nabla} n(\boldsymbol{r})}, \qquad (100)$$

where $V^{\rm XC}(\boldsymbol{r}) \equiv V^{\rm XC}\left[n,\boldsymbol{\nabla}n\right](\boldsymbol{r})$. Since $V^{\rm XC}$ is a periodic function, we can express its non-equivalent matrix elements in the real-space basis defined by Eqs. (4) and (2) as the derivative

$$V_u^{\rm XC} = \frac{\partial E_{\rm XC}}{\partial D^{\bar{u}}}. \qquad (101)$$

Applying the chain rule

$$\frac{\partial E_{\rm XC}}{\partial D^{\bar{u}}} = \int_{\mathbb{R}^3} \frac{\delta E_{\rm XC}}{\delta n(\boldsymbol{r})} \frac{\partial n(\boldsymbol{r})}{\partial D^{\bar{u}}}d^3\boldsymbol{r}, \qquad (102)$$

and the identity

$$\Omega_u(\boldsymbol{r}) = \frac{\partial n(\boldsymbol{r})}{\partial D^{\bar{u}}}, \qquad (103)$$

yields

$$V_u^{\rm XC} = \int_{\mathbb{R}^3} V^{\rm XC}(\boldsymbol{r})\Omega_u(\boldsymbol{r})d^3\boldsymbol{r}. \qquad (104)$$

Because the integral in Eq. (104) is handled numerically, it is more convenient to use integration by parts to apply the derivative in the expression for $V^{\rm XC}(\boldsymbol{r})$ in Eq. (100) to the overlap distribution Ω_u. Let us denote

$$V_{\rm XC}^0(\boldsymbol{r}) \equiv \frac{\partial \varepsilon_{\rm XC}}{\partial n(\boldsymbol{r})}, \qquad V_{\rm XC}^i(\boldsymbol{r}) \equiv \frac{\partial \varepsilon_{\rm XC}}{\partial \left(\nabla_i n(\boldsymbol{r})\right)}, \qquad (105{\rm a})$$

$$\Omega_{u,0}(\boldsymbol{r}) \equiv \Omega_u(\boldsymbol{r}), \qquad \Omega_{u,i}(\boldsymbol{r}) \equiv \nabla_i \Omega_u(\boldsymbol{r}), \qquad (105{\rm b})$$

for $i = x, y, z$. Eq. (104) can then be written as

$$V_u^{\rm XC} = \int_{\mathbb{R}^3} V_{\rm XC}^\alpha(\boldsymbol{r})\Omega_{u,\alpha}(\boldsymbol{r})d^3\boldsymbol{r}, \qquad (106)$$

where $\alpha = 0, x, y, z$. To arrive at a working expression for the XC potential, we insert the weight functions into Eq. (106), and get

$$V_u^{\rm XC} = \int_{\mathbb{R}^3} V_{\rm XC}^\alpha(\boldsymbol{r})\Omega_{u,\alpha}(\boldsymbol{r}) \sum_{A\boldsymbol{m}'} w_A(\boldsymbol{r}-\boldsymbol{m}')d^3\boldsymbol{r}.$$

It follows that the XC potential becomes

$$V_u^{\rm XC} = \sum_{A\boldsymbol{m}'} \int_{\mathbb{R}^3} V_{\rm XC}^\alpha(\boldsymbol{r})\Omega_{u,\alpha}(\boldsymbol{r}+\boldsymbol{m}')w_A(\boldsymbol{r})d^3\boldsymbol{r}. \qquad (107)$$

III. IMPLEMENTATION DETAILS

We have implemented the method described in Section II in the 4c RESPECT[88] program package. Matrix representations of operators in real space are obtained by evaluating the integrals in Eqs. (16) over the RKB Cartesian GTOs using the highly efficient and vectorized integral library INTEREST.[98] The entire implementation is parallelized using the OpenMP application programming interface to allow for multithreaded execution of the program on shared memory architectures.

Before proceeding to the main self-consistent field (SCF) procedure, i.e. the iterative solution of Eq. (11), we perform these steps:

- Exploit the exponential decay of a product of two GTOs $\chi_{\mu\mathbf{0}}^{\dagger}\chi_{\mu'\mathbf{m}}$ as their centers become more distant in order to generate a *finite* list of significant 4c overlap distributions.

- Form an array of NF unit cells.

- Calculate and store the infinite lattice sums $\Lambda_{lm,jk}$ of the interaction tensor in Eq. (83) using the procedure described in Section II F.

- Evaluate the 4c overlap matrix in reciprocal space using Eqs. (12b) and (15) and compose a unitary matrix $L(\mathbf{k}) = \left(X^{\dagger}S(\mathbf{k})X\right)^{-1/2}$ that transforms the Cartesian GTOs to orthonormalized spherical GTOs. X denotes here the the Cartesian-to-spherical transformation matrix.

During the SCF cycle, operators depending on the density matrix must be reevaluated. The most time-consuming part is the computation of the 2-electron Coulomb integrals in Eq. (74c) for $\mathbf{n}$ restricted to the NF unit cells. Therefore, we employ a variety of approximations and estimates to facilitate this step. First, centering the multipole expansion at the center of the overlap distribution Ω_u that indexes the Fock matrix, enabling us to approximate many integrals within the NF using the multipole expansion

$$J_u^e(\mathbf{n}) \approx q_u^T(\mathbf{P})\Theta(\mathbf{n} - \mathbf{P})Q, \qquad (108)$$

where $\mathbf{P}$ is the center of Ω_u, and

$$q_u^{lm}(\mathbf{P}) = -\int_{\mathbb{R}^3} \Omega_u(\mathbf{r})R^{lm}(\mathbf{r} - \mathbf{P})d^3\mathbf{r}, \qquad (109)$$

is the translated electronic multipole moment operator. Second, we apply the quaternion adaptation of the Cauchy–Schwarz inequality to obtain an upper estimate of the remaining 2-electron integrals, discarding integrals that contribute negligibly to the Fock matrix. Details of this integral screening will be published elsewhere.[86] Finally, the 2-electron integrals that contain a product of two small-component overlap distributions $\Omega_u^{SS}(\mathbf{r}_1) = \chi_{\mu\mathbf{0}}^{SS\dagger}(\mathbf{r}_1)\chi_{\mu'\mathbf{m}}^{SS}(\mathbf{r}_1)$ and $\Omega_v^{SS}(\mathbf{r}_2) = \chi_{\nu\mathbf{0}}^{SS\dagger}(\mathbf{r}_2)\chi_{\nu'\mathbf{n}'}^{SS}(\mathbf{r}_2)$ are

only computed if: 1) the bra basis function $\mu\mathbf{0}$ shares the same center with the ket basis function $\mu'\mathbf{m}$; and 2) the bra basis function $\nu\mathbf{0}$ shares the same center with the ket basis function $\nu'\mathbf{n}'$. We tested and tuned these approximations to ensure that the quality of results is not affected.

To include the XC contributions to the potential and the energy, we calculate the electronic density

$$n(\mathbf{r}) = \sum_{\mathbf{n}} \text{Tr}\left[\Omega_u(\mathbf{r} - \mathbf{n})D^{\bar{u}}\right], \qquad (110)$$

and its gradients on the grid (see Section II G), where the trace is expressed as in Eq. (69). The XC potential and its derivatives $v^{\alpha}(\mathbf{r})$ are obtained from the XCFUN library[121] and used to construct the XC Fock matrix elements in Eq. (107).

The Coulomb and XC contributions are used to assemble the nonzero real-space quaternion components of the Fock matrix in Eq. (14), which are then transformed to $\mathbf{k}$-space, evaluating the Fourier series in Eq. (59). The 4c $\mathbf{k}$-space Fock matrix is composed using Eq. (61). The kinetic operator is added in a similary way. The orthonormal basis representation of the Fock matrix is obtained as $F(\mathbf{k}) \rightarrow L^{\dagger}(\mathbf{k})F(\mathbf{k})L(\mathbf{k})$. The Fock matrix is diagonalized, and from its band energies $\varepsilon_p(\mathbf{k})$, an occupation vector $f_p(\mathbf{k})$ is formed [Eq. (19)]. The $\mathbf{k}$-space density matrix is obtained in the orthonormal basis according to Eq. (21), and transformed as $D(\mathbf{k}) \rightarrow L(\mathbf{k})D(\mathbf{k})L^{\dagger}(\mathbf{k})$.

The new density matrix in real space $D^{\mu\mathbf{m},\mu'\mathbf{0}}$ is constructed by calculating the integral in Eq. (23) over the first Brillouin zone. The integral is approximated by a sum over a Γ-centered uniform grid of $\mathbf{k}$-points with equal weights $|\mathcal{K}|/\mathcal{N}$, where $\mathcal{N}$ is the total number of sampled $\mathbf{k}$-points. Specifically, let $\mathbf{b}_i$ denote the primitive vectors in reciprocal space for $i = 1, \ldots, d$. Then the grid consists of $\mathbf{k}$-points defined as

$$\mathbf{k} = \sum_{i=1}^{d} \frac{k_i}{\mathcal{N}_i}\mathbf{b}_i, \quad k_i = -\frac{\mathcal{N}_i - 1}{2}, \ldots, \frac{\mathcal{N}_i - 1}{2}, \quad (111)$$

where $\mathcal{N}_i$ is the total number of $\mathbf{k}$-points in the i-th crystallographic direction. Such an integration scheme does not capture the discontinuity of the integrand at the Fermi surface arising in metallic systems. However, in this work we study systems with a nonzero band gap, and the integration scheme proved sufficiently accurate.

In order to accelerate the SCF convergence, we extrapolate the real-space Fock matrix using the linear combination of Fock matrices from the current and the previous SCF cycles, before transforming it to reciprocal space. The extrapolation coefficients are determined from the direct inversion of the iterative subspace (DIIS) procedure of Pulay,[122,123] applied only to the Γ-point ($\mathbf{k} = \mathbf{0}$), i.e. using error vectors defined as $e = [F(\mathbf{0}), D(\mathbf{0})]$ (in the orthonormal basis). Such a restriction has been demonstrated to be satisfactory for solid-state calculations.[85,124,125]

IV. RESULTS

To asses the performance of our methodology, we have performed calculations of the energy gaps at different k-points for the 3-dimensional silver halides (AgX, X=Cl, Br, I) using both the fully-relativistic 4c and the non-relativistic 1-component (1c) density functional level of theory. The ionic AgX crystals are known to display large scalar-relativistic effects, but with only a minor SOC.[74,76] To better assess how well our approach can treat SOC effects, we also study the 2-dimensional graphene-like honeycomb structures of silicene and germanene,[26] and SOC effects in particular.

All relativistic calculations were performed using a Gaussian finite nucleus model, as described by Visscher and Dyall.[126] The finite nucleus model is required in order to regularize the singularity of the small-component wave function evaluated at nucleif when point nuclei as this is otherwise difficult to capture with a finite basis set and point-like nuclei.

A. Silver halide crystals

We have performed calculations on the silver halide crystals in their NaCl-type FCC crystal phase. Equilibrium lattice constants are taken from the recent work of Zhao *et al.*.[74] In this work, they calculated the band gaps of the silver halides at the 2c level of the theory using STOs, and we will use their results as a reference for our calculations. We employed nonrelativistic XC functionals: the LDA-type functional SVWN5[127,128] and the GGA-type functional PBE.[129] The numerical integration required for the XC contributions was performed on a grid consisting of 302 angular points for each atom, 80 radial points for the Ag atoms, and 70 radial points for the halide atoms. Reciprocal space integration was evaluated on a uniform mesh of $7 \times 7 \times 7$ k-points [Eq. (111)]. For the large component basis, we used the all-electron pob-TZVP basis set of triple-ζ quality optimized for solid-state calculations by Peintinger *et al.*;[130] we uncontracted the basis functions, as is commonly done in relativistic calculations. However, the pob-TZVP basis set does not contain basis sets for heaviest elements such as Ag and I. Therefore, we employed the uncontracted all-electron double-ζ basis sets of Dyall[131,132] for these elements. The small-component basis functions were generated on-the-fly using the RKB condition in Eq. (3b). In order to alleviate the convergence problems that often hamper solid-state calculations due to diffuse functions in the basis sets,[75,130,133] we modified the Dyall's double-ζ basis set by deleting the most diffuse s and diffuse p function on Ag, both having exponents < 0.05 in atomic units.

Table I shows our results of the 4c and 1c calculations of the energy gaps for the AgX systems. The vertical (direct) band gaps are obtained at a set of special k-points: Γ, L, and X. The results show that the ionic AgX compounds are indirect semi-conductors, with the band gap

TABLE I. Energy band gaps of 3-dimensional AgX systems obtained for various k-points and XC functionals at the fully-relativistic 4c and nonrelativistic 1c level of theory. Equilibrium lattice constants (a_0) are taken from Ref. 74. Numbers in parenthis have been taken from Ref. 74. Note that the relativistic results of Ref. 74 have been obtained at the 2c X2C level of theory.

		gap (eV)			
AgCl	a_0 (Å)	L–L	Γ–Γ	X–X	L–Γ
LDA-1c	5.421	4.48	3.80	5.39	1.42
		(4.05)	(3.72)	(5.16)	(1.37)
LDA-4c	5.354	3.99	3.32	4.13	0.59
		(3.58)	(3.32)	(3.91)	(0.58)
PBE-1c	5.692	5.18	3.53	5.45	1.74
		(4.72)	(3.44)	(5.29)	(1.67)
PBE-4c	5.612	4.67	2.95	4.20	0.89
		(4.27)	(2.99)	(4.03)	(0.88)
AgBr	a_0 (Å)	L–L	Γ–Γ	X–X	L–Γ
LDA-1c	5.661	4.04	3.34	4.75	1.48
		(3.70)	(3.20)	(4.74)	(1.31)
LDA-4c	5.586	3.44	2.49	3.57	0.38
		(3.15)	(2.43)	(3.56)	(0.29)
PBE-1c	5.937	4.76	3.15	4.83	1.77
		(4.31)	(2.97)	(4.81)	(1.57)
PBE-4c	5.843	4.13	2.34	3.67	0.70
		(3.77)	(2.25)	(3.67)	(0.60)
AgI	a_0 (Å)	L–L	Γ–Γ	X–X	L–X
LDA-1c	5.998	4.44	3.62	3.66	1.06
		(3.38)	(3.52)	(3.66)	(1.06)
LDA-4c	5.901	3.45	2.18	2.82	-0.10
		(2.62)	(2.17)	(2.84)	(-0.08)
PBE-1c	6.280	5.12	3.28	3.58	1.62
		(3.91)	(3.14)	(3.56)	(1.60)
PBE-4c	6.169	4.14	1.96	2.75	0.50
		(3.17)	(1.90)	(2.76)	(0.49)

occurring between the L and Γ points for AgCl and AgBr, and between the L and X points for AgI. This agrees with the findings of previous studied.[74,76] All band gaps are signficantly reduced when including relativistic effects. Overall, our results agree well with those presented in Ref. 74; we reproduce the general trends as well as the difference between the relativistic and the nonrelativistic calculations.

Notable exceptions to the agreement with Ref. 74 are the L–L direct gaps, particularly those of AgI. Therefore, we conducted additional tests at the 1c level with the PBE functional, and found these differences to originate in the different basis sets used. Table II contains results obtained with the uncontracted Dyall's double-ζ (DZ), the valence double-ζ (VDZ), and the valence triple-ζ (VTZ) basis sets. We tested the original (molecular) basis sets, where we kept the diffuse exponents, as well as the reduced versions (denoted with an 'r' in front of the basis name), where we have deleted diffuse exponents smaller than 0.1 (in atomic units). The discrepancies remain also with the larger rVDZ and rVTZ basis sets, as long as the diffuse exponents are not included, and in

TABLE II. Nonrelativistic 1c energy band gaps of 3-dimensional AgX systems calculated with different basis sets. All results are obtained with the PBE functional. Comparisons are made with non-relativistic literature values obtained using either STOs and plane waves and taken from Ref. [74].

	gap (eV)			
AgCl	L–L	Γ–Γ	X–X	L–Γ
rVDZ	5.22	3.51	5.41	1.72
rVTZ	5.23	3.60	5.35	1.83
VDZ	-	-	-	-
STO, Ref. [74]	4.72	3.44	5.29	1.67
PW, Ref. [74]	4.76	3.44	5.29	1.69
AgBr	L–L	Γ–Γ	X–X	L–Γ
rVDZ	4.96	3.07	4.86	1.67
rVTZ	4.73	3.02	4.75	1.63
DZ	4.47	2.94	4.82	1.56
VDZ	4.41	2.96	4.83	1.56
STO, Ref. [74]	4.31	2.97	4.81	1.57
PW, Ref. [74]	4.35	2.96	4.79	1.58
AgI	L–L	Γ–Γ	X–X	L–X
rDZ	5.12	3.28	3.58	1.62
rVDZ	4.87	3.30	3.60	1.62
rVTZ	4.66	3.74	3.50	1.56
DZ	3.99	3.11	3.54	1.59
VDZ	3.95	3.14	3.56	1.59
STO, Ref. [74]	3.91	3.14	3.56	1.60
PW, Ref. [74]	3.92	3.13	3.54	1.58

TABLE III. Band gaps of 2-dimensional honeycomb structures at the fully-relativistic 4c and nonrelativistic 1c level of theory. Geometries are taken from Ref. [26].

		band gap [meV]	
method	basis	silicene	germanene
PBE-1c	pob-TZVP	0.026	0.028
PBE-4c	pob-TZVP	1.548	25.1
PBE-4c	cc-pVDZ	1.596	24.3
Ref. [26]		1.55	23.9

B. Honeycomb structures

To validate our method on systems larger spin–orbit effects, we have also calculated the band structure of the heavier 2-dimensional analogues of graphene: silicene and germanene. Both systems have been found to be stable in a low-buckled hexagonal geometry,[26] contrary to the truly planar graphene. To compare our calculated the band gaps with literature values, we used the geometries from Ref. [26], and the nonrelativistic PBE functional.[129] The integration grid for the XC contributions contained 80 radial points per atom, and Lebedev quadrature grid points of an adaptive size in the angular part.[136] Reciprocal space integration was performed on a uniform grid of 31×31 k-points. We employed the uncontracted all-electron pob-TZVP[130] and cc-pVDZ[137] basis sets.

Table III collects our calculated band gaps at the 1c and 4c levels of theory at the Dirac points of the silicene and germanene . For comparison, we report in Table III also the results of Liu et al.[26] calculated using the relativistic pseudopotential PAW approach.[65] Since these graphene-like structures exhibit a quantum spin Hall effect,[25,26,28] the existence of a nonzero gap is solely due to SOC. Hence, the nonrelativistic band gaps should then be strictly zero. The numbers in Table III do not display this feature exactly, but we attribute the very small values of the nonrelativistic gaps to numerical noise. The small discrepancies between our work and Ref. [26] for the germanene gap can be caused by methodological differences in the two approaches, such as the use of a pseudopotential approximation in Ref. [26] or the basis set choice in this work. In contrast to the planar graphene, the buckled geometry of the silicene and germanene enhances the SOC effect,[26] placing silicene and germanene among materials with promising technological applications.

V. CONCLUSION AND OUTLOOK

We have presented a first-principle full-potential relativistic method and its implementation for solving the 4c Dirac–Kohn–Sham equation for periodic systems employing a local basis composed of Gaussian-type orbitals. The proposed method accounts variationally for both scalar-relativistic as well as spin–orbit effects, which allow us to study solids across the entire periodic table in a uniform

some cases the differences are even bigger for the larger rVTZ basis than for the rVDZ basis. This issue is resolved when the diffuse exponents in the original basis sets are kept, and our results agree very well with those in Ref. [74] already when the smallest DZ basis set is used. In comparison, Zhao et al.[74] adopted a Slater-type quadruple-ζ (QZ4P) basis set developed by van Lenthe and Baerends,[134] also eliminating diffuse s and p functions. Additionally, Zhao et al. claim that they tested AgCl with a DZP Slater-type basis, and the calculated band gaps were differing marginally (< 0.1 eV) from the results obtained with QZ4P. As a consequence, Zhao et al. arrive at the conclusion that the band gaps should be well converged already with the DZP basis. This is line with the findings of Te Velde and Baerends that a reasonable basis-set limit (with errors $< 10^{-3}$ a.u. in cohesive energies per atom) for densely packed systems can be reached already with a STO basis set of double-ζ quality, provided it contains polarization functions.[135] Considering that GTOs and STOs only differ in the radial part, one would expect that a similar behaviour should be seen also for GTOs. We confirmed this observation. However, great care must be taken when adopting basis sets for solid-state calculations, and we do not generally recommend deleting diffuse exponents for heavy elements. Optimized solid-state GTO basis sets have been developed by Peintinger et al.[130] for the lighter elements of the periodic table, but this work needs to be extended to the elements in the lower parts of the periodic table as well.

and consistent manner. The explicit built-in periodicity allows for a treatment of systems of arbitrary dimensionality without having to introduce nonphysical replicas of the systems studied in non-periodic dimensions. We formulated key principles of the method in the 4c Kramers-restricted framework, exploiting the time-reversal structure of operators in real and reciprocal space, and showed how to assemble the real-space Coulomb and exchange–correlation operators in this framework. We have discussed the conditionally-convergent electrostatic infinite lattice sums arising in studies of periodic systems, and we adopted the multipole expansion and an iterative renormalization procedure to calculate the lattice sums of the interaction tensor. To accelerate the calculations, some explicit 2-electron integrals were neglected based on an efficient screening scheme, or approximated with a multipole expansion. The method has been implemented in the 4c RESPECT[88] code, using the vectorized integral library INTEREST.[98] Finally, we have presented some example calculations using this methodology for 3-dimensional silver halide crystals in their FCC phase, and 2-dimensional honeycomb structures featuring the quantum spin Hall effect. Energy band gaps were calculated at various special $\boldsymbol{k}$-points. Overall, our results agreed very well with other published findings.

The methodology presented in this papers holds promise in the computational study of solid-state materials. The 4c scheme is conceptually simpler and more transparent than approximate 2c techniques, and can be used to produce reference results to benchmark more approximate methods, and in this way increase confidence in approximate schemes and thus pave the way for computational studies of more complex materials. Furthermore, the full-potential formalism adopted here enables investigations of unique features of spin–orbit coupled materials, such as magnetic response properties and core-electron (X-ray) spectroscopy, where a full relativistic description is needed. We also believe that the method can prove valuable in a search for materials with non-trivial topological properties.

Appendix A: Translation symmetry

In this appendix, we review some consequences of the translational symmetry on operators in various basis representations. We will here only be concerned with discrete translations, *i.e.* translations by an arbitrary integer-modulated lattice vector $\boldsymbol{m}$, defined by Eq. (5). Let $t_{\boldsymbol{m}}$ denote a translation operator for the lattice vector $\boldsymbol{m}$, defined by an application to a function f:

$$(t_{\boldsymbol{m}} f)(\boldsymbol{r}) \equiv f(\boldsymbol{r} - \boldsymbol{m}). \tag{A1}$$

An operator A is *translationally invariant* iff it commutes with the translation operators for all lattice vectors $\boldsymbol{m}$ ($[\cdot, \cdot]$ denotes a commutator):

$$[A, t_{\boldsymbol{m}}] = 0. \tag{A2}$$

Clearly, the momentum operator $\boldsymbol{p}$, as well as the spin operator $\boldsymbol{\sigma}$ are translationally invariant. As a consequence, the composite operators $p^2/2$ (nonrelativistic kinetic energy) and $\boldsymbol{\sigma} \cdot \boldsymbol{p}$ are also translationally invariant. For this reason, we can omit the spin- and momentum-dependence of an operator A from the following discussion without loss of generality. Let $A(\boldsymbol{r})$ be the coordinate representation of A. Translation invariance of A [Eq. (A2)] then requires

$$A(\boldsymbol{r} + \boldsymbol{m}) = A(\boldsymbol{r}). \tag{A3}$$

Matrix elements of A expressed in the discrete real-space basis of Eq. (4) are obtained as

$$A_{\mu\boldsymbol{m}, \mu'\boldsymbol{m}'} = \int_{\mathbb{R}^3} \chi_{\mu\boldsymbol{m}}^{\dagger}(\boldsymbol{r}) A(\boldsymbol{r}) \chi_{\mu'\boldsymbol{m}'}(\boldsymbol{r}) d^3\boldsymbol{r}. \tag{A4}$$

For any lattice vector $\boldsymbol{n}$, it follows, that

$$A_{\mu\boldsymbol{m}, \mu'\boldsymbol{m}'} = A_{\mu\boldsymbol{m}+\boldsymbol{n}, \mu'\boldsymbol{m}'+\boldsymbol{n}} = A_{\mu\boldsymbol{0}, \mu'\boldsymbol{m}'-\boldsymbol{m}}, \tag{A5}$$

implying that the real-space matrix elements of translationally invariant operators have a Toeplitz structure. In addition, if the operator A is Hermitian, then

$$A_{\mu\boldsymbol{0}, \mu'\boldsymbol{m}}^{\dagger} = A_{\mu'\boldsymbol{0}, \mu-\boldsymbol{m}}, \tag{A6}$$

where $A^{\dagger}$ denotes the Hermitian conjugate within the 4×4 bispinor space.

Reciprocal-space elements of A for $\boldsymbol{k}, \boldsymbol{k}' \in \mathcal{K}$ are acquired by using Eq. (6) together with Eq. (A5):

$$A_{\mu\mu'}(\boldsymbol{k}, \boldsymbol{k}') = \frac{1}{|\mathcal{K}|} \sum_{\boldsymbol{m}\boldsymbol{m}'} e^{-i\boldsymbol{k}\cdot\boldsymbol{m}} e^{i\boldsymbol{k}'\cdot\boldsymbol{m}'} A_{\mu\boldsymbol{0}, \mu'\boldsymbol{m}'-\boldsymbol{m}}.$$

Changing the summation variables yields

$$A_{\mu\mu'}(\boldsymbol{k}, \boldsymbol{k}') = \delta(\boldsymbol{k} - \boldsymbol{k}') A_{\mu\mu'}(\boldsymbol{k}), \tag{A7}$$

$$A_{\mu\mu'}(\boldsymbol{k}) = \sum_{\boldsymbol{m}} e^{i\boldsymbol{k}\cdot\boldsymbol{m}} A_{\mu\boldsymbol{0}, \mu'\boldsymbol{m}}, \tag{A8}$$

where we have employed

$$\delta(\boldsymbol{k}) \equiv \frac{1}{|\mathcal{K}|} \sum_{\boldsymbol{m}} e^{i\boldsymbol{k}\cdot\boldsymbol{m}}, \tag{A9}$$

which is the *Fourier kernel* representation of the Dirac δ-function. Notice, that the symmetry in Eq. (A5) resulted in the block-diagonal reciprocal-space matrix [Eq. (A7)]. This argument can also be reversed, *i.e.* any block-diagonal $\boldsymbol{k}$-space matrix will have a Toeplitz structure [Eq. (A5)] in real space. We have applied this argument when constructing only the nonequivalent elements of the real-space density matrix in Eq. (23). Finally, the symmetry in Eq. (A6) leads to matrices in the reciprocal space that are Hermitian for each $\boldsymbol{k}$ individually:

$$A_{\mu\mu'}^{\dagger}(\boldsymbol{k}) = A_{\mu'\mu}(\boldsymbol{k}). \tag{A10}$$

Therefore, provided that the Fock matrix in Eq. (14) satisfies the combined translational and Hermitian symmetry in Eq. (A6), the eigenvalues $\varepsilon(\boldsymbol{k})$ in Eq. (11) are guaranteed to be real.

Translational symmetry allows us to assign finite expectation values of operators that naturally describe extensive properties, such as the kinetic energy of electrons. Beginning with a divergent expression for the expectation value of a translationally invariant one-electron operator

A (given that the density matrix is translationally invariant as well), we can write

$$\langle A \rangle = \sum_{\boldsymbol{m}\boldsymbol{m}'} \text{Tr} \left[A_{\mu\boldsymbol{m},\mu'\boldsymbol{m}'} D^{\mu'\boldsymbol{m}',\mu\boldsymbol{m}} \right]$$
$$= \sum_{\boldsymbol{m}} 1 \sum_{\boldsymbol{m}'} \text{Tr} \left[A_{\mu\boldsymbol{0},\mu'\boldsymbol{m}'} D^{\mu'\boldsymbol{m}',\mu\boldsymbol{0}} \right],$$

where Tr denotes the trace in the 4×4 bispinor space. If we employ the short-hand notation from Eq. (31), and realize, that $\sum_{\boldsymbol{m}} 1 \equiv N$ is the total (infinite) number of unit cells, we can calculate the expectation value of A *per unit cell* in the thermodynamic limit ($N \to \infty$) as

$$\frac{\langle A \rangle}{N} = \text{Tr} \left[A_u D^{\bar{u}} \right]. \tag{A11}$$

Appendix B: Spherical multipole expansion

Here we summarize the formulation of the spherical multipole expansion needed to evaluate the far-field contribution to the Coulomb operator. We follow the framework of Helgaker *et al.*[111] and Watson *et al.*[110] The Coulomb interaction operator $|\boldsymbol{r}_1 - \boldsymbol{r}_2|^{-1} \equiv r_{12}^{-1}$ can be expanded (as a function of 6 variables) around an arbitrary center $(\boldsymbol{P}, \boldsymbol{Q})$ into a spherical multipole expansion which takes the form

$$\frac{1}{r_{12}} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \sum_{j=0}^{\infty} \sum_{k=-j}^{j} R^{lm}(\boldsymbol{r}_1 - \boldsymbol{P}) \Theta_{lm,jk}(\boldsymbol{Q} - \boldsymbol{P}) R^{jk}(\boldsymbol{r}_2 - \boldsymbol{Q}), \tag{B1}$$

where

$$\Theta_{lm,jk}(\boldsymbol{R}) = (-1)^j I_{l+j,m+k}^*(\boldsymbol{R}), \tag{B2}$$

is the *interaction tensor*, $R^{lm}(\boldsymbol{r})$ and $I_{lm}(\boldsymbol{r})$ are the *scaled regular* and *scaled irregular solid harmonics*, respectively, defined as

$$R^{lm}(\boldsymbol{r}) = \frac{1}{\sqrt{(l-m)!(l+m)!}} r^l C_{lm}(\vartheta, \varphi), \tag{B3}$$

$$I_{lm}(\boldsymbol{r}) = \sqrt{(l-m)!(l+m)!} r^{-l-1} C_{lm}(\vartheta, \varphi). \tag{B4}$$

Here $C_{lm}(\vartheta, \varphi)$ are eigenfunctions of the angular momentum operators L^2, L_z, namely the *spherical harmonics* in Racah's normalization, obtained from the conventional spherical harmonics $Y_{lm}(\vartheta, \varphi)$ as

$$C_{lm}(\vartheta, \varphi) = \sqrt{\frac{4\pi}{2l+1}} Y_{lm}(\vartheta, \varphi). \tag{B5}$$

We shall use the compact matrix notation

$$\frac{1}{r_{12}} = R^T(\boldsymbol{r}_1 - \boldsymbol{P}) \Theta(\boldsymbol{Q} - \boldsymbol{P}) R(\boldsymbol{r}_2 - \boldsymbol{Q}), \tag{B6}$$

where R is a vector and Θ is a matrix defined by their respective elements R^{lm} and $\Theta_{lm,jk}$. The series in Eq. (B6) is convergent for all points $(\boldsymbol{r}_1, \boldsymbol{r}_2)$ that satisfy the condition

$$|\boldsymbol{r}_1 - \boldsymbol{r}_2 + \boldsymbol{Q} - \boldsymbol{P}| < |\boldsymbol{Q} - \boldsymbol{P}|. \tag{B7}$$

The scaled regular and irregular solid harmonics have the following properties ($\lambda \in \mathbb{R}$ is an arbitrary scaling factor):

$$R^{l-m}(\boldsymbol{r}) = (-1)^m R^{lm*}(\boldsymbol{r}), \tag{B8a}$$

$$I_{l-m}(\boldsymbol{r}) = (-1)^m I_{lm}^*(\boldsymbol{r}), \tag{B8b}$$

$$R^{lm}(\lambda\boldsymbol{r}) = \lambda^l R^{lm}(\boldsymbol{r}), \tag{B8c}$$

$$I_{lm}(\lambda\boldsymbol{r}) = \frac{1}{|\lambda|} \frac{1}{\lambda^l} I_{lm}(\boldsymbol{r}). \tag{B8d}$$

The regular solid harmonics obey the addition theorem

$$R^{lm}(\boldsymbol{r} - \boldsymbol{P}) = \sum_{j=0}^{l} \sum_{k=-j}^{j} R_{l-j,m-k}(-\boldsymbol{P}) R^{jk}(\boldsymbol{r}), \tag{B9}$$

which can be written in the following matrix form

$$R(\boldsymbol{r} - \boldsymbol{P}) = W(\boldsymbol{P})R(\boldsymbol{r}), \qquad (B10)$$

where W is the *translation tensor*, its elements defined as

$$W_{lm,jk}(\boldsymbol{P}) = R_{l-j,m-k}(-\boldsymbol{P}). \qquad (B11)$$

The translation tensor W can be used to evaluate the regular solid harmonics for shifted arguments. Moreover, we can apply Eq. (B10) to derive a similar rule for the interaction tensor. Multipole expansions of r_{12}^{-1} expanded around 2 different centers $(\boldsymbol{P}, \boldsymbol{Q})$ and $(\bar{\boldsymbol{P}}, \bar{\boldsymbol{Q}})$ must coincide, so that

$$\begin{aligned}
\frac{1}{r_{12}} &= R^T(\boldsymbol{r}_1 - \boldsymbol{P})\Theta(\boldsymbol{Q} - \boldsymbol{P})R(\boldsymbol{r}_2 - \boldsymbol{Q}) \\
&= R^T(\boldsymbol{r}_1 - \bar{\boldsymbol{P}})\Theta(\bar{\boldsymbol{Q}} - \bar{\boldsymbol{P}})R(\boldsymbol{r}_2 - \bar{\boldsymbol{Q}}).
\end{aligned}$$

Applying the addition theorem [Eq. (B10)], we identify

$$\Theta(\boldsymbol{Q} - \boldsymbol{P}) = W^T(\bar{\boldsymbol{P}} - \boldsymbol{P})\Theta(\bar{\boldsymbol{Q}} - \bar{\boldsymbol{P}})W(\bar{\boldsymbol{Q}} - \boldsymbol{Q}). \quad (B12)$$

Using $W(\boldsymbol{0}) = \mathbb{I}$, and setting $\bar{\boldsymbol{P}} = \boldsymbol{P}$ and $\bar{\boldsymbol{Q}} = \boldsymbol{P} + \boldsymbol{Q}$ in Eq. (B12), we obtain the corollary

$$\Theta(\boldsymbol{Q} - \boldsymbol{P}) = \Theta(\boldsymbol{Q})W(\boldsymbol{P}). \qquad (B13)$$

In the present implementation we avoid using complex numbers for multipole expansions by expressing interaction and translation tensors in terms of the real (regular and irregular) solid harmonics, which we construct from recurrence equations (see Ref. 111) and we do therefore not evaluate the zero imaginary part of the real-valued Coulomb r_{12}^{-1} operator.

Appendix C: Lattice sum of interaction tensors

Here we prove the recurrence relation in Eq. (89), establishing a rapidly convergent scheme for the computation of lattice sums of spherical interaction tensors. Let us begin by fragmenting the far-field (FF) into layers FF_r as follows: Let the near-field (NF) be a block consisting of unit cells with indices $n^i = -N_i, \ldots, N_i$ for each of the periodic dimensions $i = 1, \ldots, d$. For generic non-cubic lattices, such an object has a diamond-like shape. The first layer of the far-field, FF_1, envelopes the NF by placing supercells in all directions, each supercell having as many unit cells as the NF itself. The process is then repeated for the next layer of the far-field, FF_2, with the exception that the supercell now contains all unit cells in both NF and FF_1, as depicted in the following scheme:

$$\ldots \mid \underbrace{\overline{-3N_i - 1 \ldots - N_i - 1}}_{2N_i+1} \mid \underbrace{\overline{-N_i \ldots - 1}\boxed{0}\overline{1 \ldots N_i}}_{2N_i+1} \mid \underbrace{\overline{N_i + 1 \ldots 3N_i + 1}}_{2N_i+1} \mid \underbrace{\overline{3N_i + 2 \ldots 9N_i + 4}}_{2(3N_i+1)+1} \mid \ldots \qquad (C1)$$

(with labels FF_1, NF, NF, FF_1, FF_2 above respective groups)

Let N_{ir} denote the upper extent of the far-field layer r in the direction i, *i.e.* it is the index of the unit cell that is the farthest from the center 0. Then N_{ir} satisfies the following recurrence relations ($r = 0$ labels the NF)

$$\begin{aligned}
N_{i0} &= N_i, \\
N_{ir+1} &= 3N_{ir} + 1,
\end{aligned} \qquad (C2)$$

which have the solution

$$N_{ir} = \frac{(2N_i + 1)3^r - 1}{2}. \qquad (C3)$$

The number of unit cells in layer r is given by

$$|FF_r| = 3^{d(r-1)}(3^d - 1)|NF|, \qquad (C4)$$

where $|X|$ denotes the number of elements of X. From Eq. (C4), we can see that the sizes of the layers form a geometric sequence. Therefore, the partitioning in Eq. (C1) divides the space into regions that become exponentially larger with each new layer. Formally, we define FF_r as

$$FF_r = \left\{ (n^1 \ldots n^d) \in \mathbb{Z}^d; 1 \le \max_{i=1\ldots d}\left(\frac{|n^i| - 1}{N_{ir-1}}\right) \le 3 \right\}. \qquad (C5)$$

The overall far-field is then given by the union

$$FF = \bigcup_{r=1}^{\infty} FF_r, \qquad (C6)$$

and the lattice sum in Eq. (83) becomes

$$\Lambda = \sum_{\boldsymbol{n} \in FF} \Theta(\boldsymbol{n}) = \lim_{t \to \infty} \sum_{r=1}^{t} \sum_{n \in FF_r} \Theta(n^i \boldsymbol{a}_i),$$

where we have abbreviated the summation indices as $n = (n^1 \ldots n^d)$. It follows, that the lattice sum is obtained as a limit of partial sums

$$\Lambda = \lim_{t \to \infty} \Lambda^t, \qquad (C7)$$

$$\Lambda^t = \sum_{r=1}^{t} \sum_{n \in FF_r} \Theta(n^i \boldsymbol{a}_i). \qquad (C8)$$

Let us consider the term $t + 1$:

$$\Lambda^{t+1} = \Lambda^1 + \sum_{r=2}^{t+1} \sum_{n \in \mathrm{FF}_r} \Theta(n^i \boldsymbol{a}_i)$$

$$= \Lambda^1 + \sum_{r=1}^{t} \sum_{n \in \mathrm{FF}_{r+1}} \Theta(n^i \boldsymbol{a}_i). \quad \text{(C9)}$$

The following identity relates the two sums over different layers of the far-field

$$\sum_{n \in \mathrm{FF}_{r+1}} \Theta(n^i \boldsymbol{a}_i) = \sum_{n \in \mathrm{FF}_r} \sum_{\mu \in \mathcal{P}} \Theta\left((3n^i - \mu^i)\boldsymbol{a}_i\right), \quad \text{(C10)}$$

where $\mathcal{P}$ is the Cartesian power

$$\mathcal{P} = \{-1, 0, 1\}^d,$$

for $d = 3, \mathcal{P} = \{(\pm 1, \pm 1, \pm 1), (\pm 1, \pm 1, 0), \ldots\}$ and contains the reference unit cell and all its 26 nearest neighbours.

Up to this point, the proof has been of a general nature – we did not need to specify Θ or use its properties. However, in order to obtain an applicable recursive formulation, we need to express the term Λ^{t+1} via the previous terms. To proceed, we therefore apply the addition theorem in Eq. (B13), factorizing the interaction tensor as

$$\Theta\left((3n^i - \mu^i)\boldsymbol{a}_i\right) = \Theta\left(3n^i \boldsymbol{a}_i\right) W\left(\mu^i \boldsymbol{a}_I\right)$$

$$\equiv \mathcal{U}\left[\Theta\left(n^i \boldsymbol{a}_i\right)\right] W\left(\mu^i \boldsymbol{a}_i\right),$$

where W is the translation tensor [Eq. (B11)], and where we have defined the scaling operator $\mathcal{U}$ as

$$\mathcal{U}\left[\Theta_{lm,jk}(\boldsymbol{n})\right] \equiv \Theta_{lm,jk}(3\boldsymbol{n}) = \frac{1}{3^{l+j+1}} \Theta_{lm,jk}(\boldsymbol{n}). \quad \text{(C11)}$$

Here we applied the scaling property of the irregular solid harmonics [Eq. (B8d)]. Returning to Eq. (C9), this leads to

$$\Lambda^{t+1} = \Lambda^1 + \sum_{r=1}^{t} \sum_{n \in \mathrm{FF}_r} \sum_{\mu \in \mathcal{P}} \Theta\left((3n^i - \mu^i)\boldsymbol{a}_i\right)$$

$$= \Lambda^1 + \mathcal{U}\left[\sum_{r=1}^{t} \sum_{n \in \mathrm{FF}_r} \Theta\left(n^i \boldsymbol{a}_i\right)\right] \sum_{\mu \in \mathcal{P}} W\left(\mu^i \boldsymbol{a}_i\right).$$

If we define the aggregate translation matrix

$$\mathcal{W} = \sum_{\mu \in \mathcal{P}} W\left(\mu^i \boldsymbol{a}_i\right) \equiv \sum_{\mu^1 \ldots \mu^d = -1}^{1} W(\mu^i \boldsymbol{a}_i), \quad \text{(C12)}$$

then

$$\Lambda^{t+1} = \Lambda^1 + \mathcal{U}\left(\Lambda^t\right) \mathcal{W}, \quad \text{(C13)}$$

which completes the proof.

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